MODULAR SYSTEM

THERMODYNAMICS

and Molecular Physics

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PREFACE

This book is about thermodynamics and molecular physics. Splitting up the word 'Thermodynamics' into 'thermo' and 'dynamics' the branch of physics it describes. It relates to the energy hidden inside matter and how it is converted into useful work.

Molecular physics is about the relationship between the 'microscopic' world of atoms and molecules, their motions, energies, and their relationship with the 'macroscopic' variables such as pressure and temperature.

The close link between these two branches of physics necessitates them being discussed together in most textbooks. Historically, the laws of thermodynamics were firmly established before many scientists even believed in the existence of atoms. Despite this, all of the phenomena in thermodynamics can be explained on the basis of atomic structure of matter.

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CHAPTER 1

Fluid Mechanics

Chapter 1 concerns fluid mechanics. Despite being a different branch of physics to thermodynamics, the concept of pressure that is developed in this chapter will prove to be very important in thermodynamics studies.

'Fluid' is a general name for the 'flowing' state of matter. Gases and liquids fall into this category. Fluid mechanics is about moving fluids, whereas fluid statics is about stationary fluids.

1.1 DENSITY

The **density** of a substance is the mass of unit volume of that substance. The density of iron, for example, is the mass of 1 m^3 of iron.

Density is defined by the formula;

$$\rho = \frac{m}{V}$$

Two commonly used units for density are $\frac{kg}{m^3}$ and $\frac{g}{cm^3}$.

For example, the density of water is $\rho_{water} = 1\ g/cm^3 = 1000\ kg/m^3$.

Example 1.1 The Mass of an iron sphere

Calculate the mass of a solid iron sphere that has a diameter of 8 cm. (Take $\rho_{iron} = 7.9\ g/cm^3$)

Solution

First find the volume,

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(4cm)^3 \cong 268cm^3$$

From the definition, the formula for mass follows

$$m = \rho V$$

$$m = \left(7.9\frac{g}{cm^3}\right)(268\ cm^3)$$

$$m \cong 2117g$$

Example 1.2 The Density of mixtures

5 g of ethyl alcohol is mixed with 5 g of water. Find the density of the mixture.

(Take $\rho_{water} = 1\ g/cm^3$, $\rho_{alcohol} = 0.8\ g/cm^3$)

Solution

Using the definition of density

$$\rho = \frac{mass}{volume} = \frac{m_{alcohol} + m_{water}}{V_{alcohol} + V_{water}}$$

$$\rho = \frac{5g + 5g}{6.25cm^3 + 5cm^3}$$ (How were the volumes of water and alcohol found?)

$$\rho = \frac{10g}{11.25cm^3} = 0.89\ g/cm^3$$

Unit Conversions

Try to remember the following conversion factors:

Area

$1m^2 = 10^2\ dm^2 = 10^4\ cm^2$

Volume

$1m^3 = 10^3\ dm^3 = 10^6\ cm^3$

By definition,

1 litre ≡ $1dm^3$,

1 millilitre = $10^{-3}\ dm^3 = 1cm^3$

The density of mercury is $13.6\ g/cm^3$. This value can be changed into kg/m^3 as follows below

$$13.6\frac{g}{cm^3} = 13.6 \times \frac{1g}{1cm^3} = 13.6 \times \frac{10^{-3}kg}{10^{-6}m^3} = 13.6 \times 10^3 \frac{kg}{m^3} = 13\ 600 \frac{kg}{m^3}$$

The two replacements in this operation are shown below;

$$1\ g = 10^{-3}\ kg \quad \text{and} \quad 1\ cm^3 = 10^{-6}\ m^3.$$

Material	ρ	
	g/cm^3	kg/m^3
Water	1.0	1000
Ice	0.92	920
Aluminum	2.7	2700
Copper	8.9	8900
Gold	19.3	19300

Table 1.1 The densities of various substances at room temperature

Density is an **intrinsic property** of a substance. Mass and volume on the other hand, are **bulk properties**. An intrinsic property of a substance (or a system) is independent of the geometric size of the substance, while bulk properties depend on the geometric size of the substance. Intrinsic and bulk properties of a substance can be compared by analogy with a bottle of water. Suppose water in a bottle is emptied by pouring it into two glasses in equal amounts. The mass and volume of water, in each of the glasses, will be half the mass and volume of water in the bottle; they are bulk properties. The water's density, on the other hand, remains unchanged; it is an intrinsic property.

1.2 PRESSURE

The concept of pressure is already familiar to us before we learn its formal definition. Common sense teaches us not to push against sharp objects with our bare hands. This is because a small force not distributed over a large area can cause a large pressure; and pain.

Pressure is defined as the (perpendicular) force per unit area (Figure 1.1).

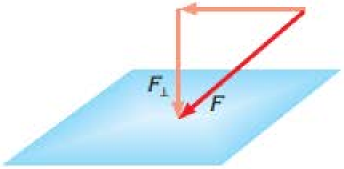


Figure 1.1 The perpendicular component of force

$$P \equiv \frac{F_\perp}{A}$$

The SI unit of pressure is the Pascal (Pa). 1 Pascal is the pressure applied by 1 Newton of force pushing over an area of $1 m^2$.

$$1\,\text{Pa} \equiv 1\frac{\text{N}}{\text{m}^2}$$

Atmospheric pressure is the pressure exerted by the weight of the gases in the atmosphere. The atmosphere is continuously 'pushing down' upon all things on Earth, including Earth's surface.

Pressure has units other than Pascal. Two of them (generally used in chemistry) are: the atmosphere (atm), and centimetres of mercury (cm-Hg). Their conversion factors are:

$$76 \text{ cm-Hg} \equiv 1 \text{ atm} \cong 10^5 \text{ Pa}.$$

1 atmosphere (or standard atmospheric pressure) is defined to be the pressure exerted by a 76 cm high mercury column. The exact pressure of 76 cm-Hg is about 101 325 Pa, but generally the approximate - and easier to remember - value 10^5 Pa (=100 kPa) will be used. Atmospheric pressure will be denoted by P_0.

The atmospheric pressure at a location, is caused by the weight of the atmosphere above that location. This means that atmospheric pressure changes with altitude and weather conditions, as indicated in Figure 1.2.

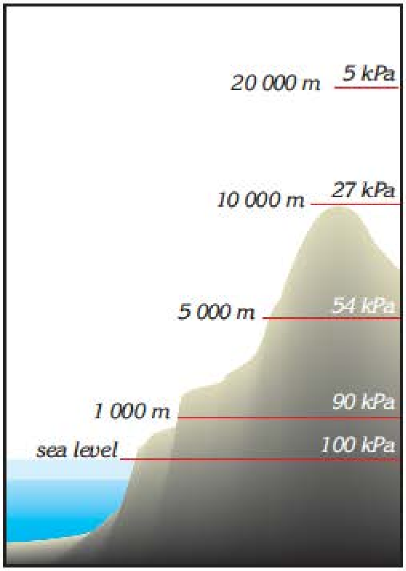


Figure 1.2 The change of atmospheric pressure with altitude

Liquid Pressure

When struck by a hammer, a nail exerts the same force upon the wall, in the same direction as the hammer as shown in Figure 1.3. Solids transmit the force applied upon them without changing direction. The case is different for liquids and gases.

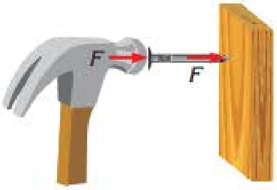


Figure 1.3 Solids transmit force in the same direction

Liquids (in equilibrium) transmit pressure equally in all directions, as shown in Figure 1.4. This statement is known as **Pascal's principle**. This can be checked by pressing a water- filled elastic balloon with your finger.

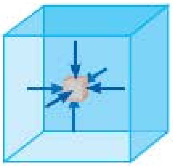


Figure 1.4 Liquids apply pressure in all directions

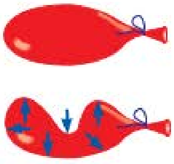


Figure 1.5 Liquids transmit pressure in all directions

Instead of producing a finger-shaped protrusion on the other side, the balloon will expand in all directions because the pressure caused by the finger is transmitted in all directions. This is illustrated in Figure 1.5.

Variation of Liquid Pressure with Depth

Think about a container filled with water. Water pushes against the surfaces of the container, but cannot apply a force sideways along the surfaces. The force exerted by a stationary liquid is perpendicular to the surfaces of the container at all points, as shown in Figure 1.6.

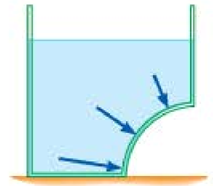


Figure 1.6 Liquid pressure is perpendicular to the surfaces of the container

The liquid pressure at the bottom of a container, caused by the weight of the liquid can be found. Consider a cylindrical container, as in Figure 1.7;

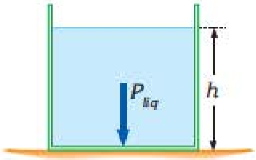


Figure 1.7 The pressure at the bottom is caused by the weight of the liquid

$$P_{liq} = \frac{F}{A} = \frac{\text{Weight of liquid}}{A} = \frac{mg}{A} = \frac{\rho Vg}{A} = \frac{\rho Ahg}{A}$$

$$P_{liquid} = \rho gh$$

By carrying out a dimensional analysis of the units:

$$\frac{kg}{m^3} \times \frac{N}{kg} \times m = \frac{N}{m^2} = Pa$$

Though we used a cylindrical shaped container for the derivation, the formula can be used for any container as discussed below.

Three points must be noted when using the liquid pressure formula:

- The formula does not express the *total* pressure at the bottom of the container. To find the total pressure at the bottom of the container, the atmospheric pressure, pushing from above the surface of the liquid, must be added to the pressure applied by the weight of the liquid, as shown in Figure 1.8.

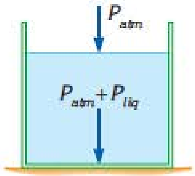


Figure 1.8 The total pressure at the bottom

- The 'h' in the formula indicates the depth below the surface, not the height above the bottom, as shown in Figure 1.9. Beneath a submarine, in an ocean, there may be thousands of metres to the ocean floor, but the water pressure acting on the submarine is caused by the weight of water above it.

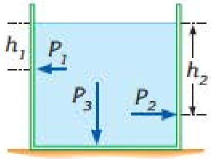


Figure 1.9 The height, h is measured from the surface

- A direct result of combining Pascal's principle into the liquid pressure formula: The pressure in a stationary liquid is the same at all points of the same depth. In other words, pressure in a stationary liquid changes only with depth.

In Figure 1.10, the water column directly above the point of application of pressure P_1 does not mean that P_1 is greater than the pressure, P_2. Pressure in a liquid is transmitted around corners. Thus, the weight of the water column is supported by all the bottom of the container, not just by the section directly below the column.

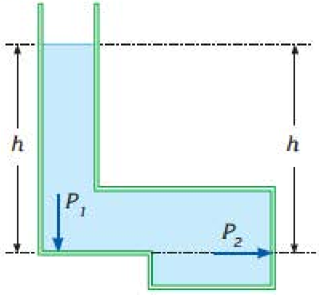


Figure 1.10 $P_1=P_2$ since the vertical heights from the top of the surface are the same. Pressure in a liquid can 'turn around the corners'

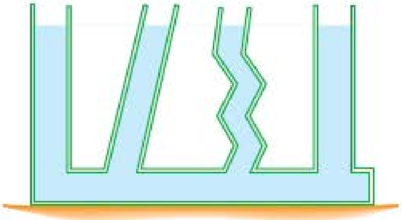


Figure 1.11 The height of water in a column is independent of the amount of water in the column

The Combined vessels from 'First Step in Physics' is a suitable example to demonstrate the facts above. One such vessel is shown in Figure 1.11.

Pressure Force

Consider a cylindrical vessel filled with water. What is the force acting on the bottom and on the side walls, due to the pressure applied by the water inside?

Finding the total pressure force on the bottom is easy;

$$F_{\text{on the bottom}} = P\,A = \rho g h A$$

since the pressure is the same at all points at the bottom of the container, as indicated in Figure 1.12.

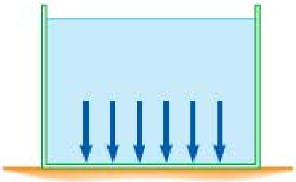


Figure 1.12 Pressure is the same at all points at the bottom

To find the pressure force applied by the liquid on one side of the container, the following problem must be considered: The pressure increases with depth below the water surface, as shown in Figure 1.13, starting from zero near the surface and reaching its maximum value at the bottom. Which value of pressure must be used to calculate the net force?

The value of pressure resulting in the correct net force, when used in the formula

$$F = PA$$

is the *average* value of pressure.

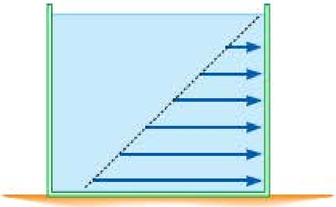


Figure 1.13 The pressure on the side walls change with depth.

Calculating the average value of pressure is not difficult, since pressure increases *uniformly* with depth, as shown in Figure 1.13. If a quantity is changing uniformly, its average value is given by

$$\text{average} = \frac{\text{min} + \text{max}}{2}$$

Therefore

$$F_{\text{side wall}} = P_{\text{av}} \times A_{\text{side wall}} = \left(\frac{P_{\min} + P_{\max}}{2}\right) A_{\text{side wall}} = \left(\frac{0 + \rho g h}{2}\right) A_{\text{side wall}}$$

$$F_{\text{side wall}} = \left(\frac{\rho g h}{2}\right) A_{\text{side wall}}$$

Example 1.3 Force on a submarine

A submarine is submerged 30 m under the surface of the sea. What is the pressure force on one of the door covers of area 3 m^2? Take air pressure as $P_0 = 1$ atm, $\rho_{\text{water}} \approx 1000\ \text{kg/m}^3$ and $g \approx 10\text{N/kg}$. (Actually the density of sea water is greater than that of pure water due to the dissolved salt dissolved in it)

Solution

The total pressure at 30 m below the sea surface is the sum of the liquid and atmospheric pressures: $P = P_{\text{water}} + P_0$

$$P = \rho g h + P_0$$

$$P = (1000\frac{kg}{m^3})(10\frac{N}{kg})(30\ m) + (1\ Atm)$$

$$P = 300\ 000\ Pa + 100\ 000\ Pa$$

$$P = 400\ 000\ Pa = 400\ kPa$$

Force exerted over the door cover from outside due to this pressure is

$$F = P\,A$$

$$F = (4\times10^5\ Pa)\ (3\ m^2)$$

$$F = 12\times10^5\ N = 1\ 200\ kN$$

This force tries to push the door cover inside, as shown in Figure 1.14.

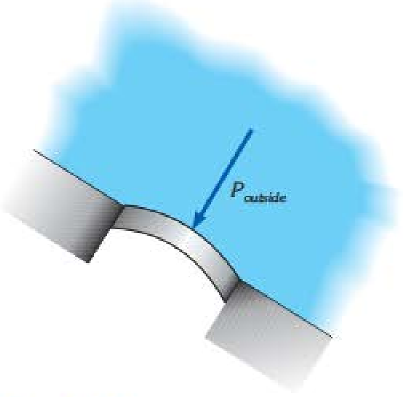


Figure 1.14 The outside pressure is the combined effect of the atmospheric pressure and the water pressure

Hydraulic Lever

The hydraulic lever takes advantage of Pascal's principle to lift heavy objects with a small force. The working principle is to apply the same pressure over different areas. In Figure 1.15, the pressures at points A and B must be equal, because both points are at the same level. (Remember the pressure in a stationary liquid is the same at all points of the same depth)

$$P_A = P_B$$

$$\frac{F_1}{A_1} = \frac{F_2}{A_2}$$

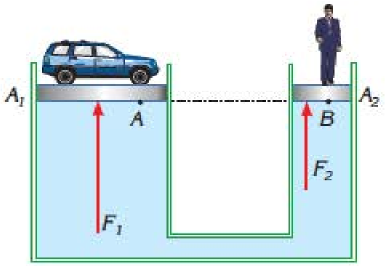


Figure 1.15 The hydraulic lever

Pressure Measurements

The first vacuum on Earth was produced by Torricelli in 1642. He used a bowl of mercury and a long glass tube, sealed at one end, to measure atmospheric pressure. Consider Figure 1.16; when the pressure of the mercury column acting downward equals the atmospheric pressure, equilibrium is reached. A vacuum is left behind at the top of the mercury column. Before this the common scientific belief was that the existence of a vacuum was impossible, because nature 'hated emptiness'. The device invented by Torricelli is shown in Figure 1.16, and is generally referred as the 'common barometer' or 'mercury barometer'.

Consider the **mercury barometer** in Figure 1.16. The pressure at points A and B must be equal as they are at the same level in a liquid. Thus,

$$P_A = P_B$$

$$P_0 = P_{Hg}$$

P_0 means atmospheric pressure.

Atmospheric pressure is equal to the pressure of a mercury column in the tube. In other words;

Atmospheric pressure ~ height of mercury in the column

Therefore we can directly read the height of the column to express the open air (atmospheric) pressure. For example the atmospheric pressure can be expressed as '69 cm-Hg'.

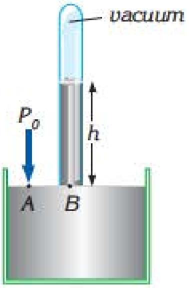


Figure 1.16 The mercury barometer

Many measurements have shown that the average value for normal atmospheric pressure at sea level, at a temperature of 0 °C corresponds to a pressure of 76 cm of mercury in the column. This is the reason for defining 1 atm to be equivalent to 76 cm-Hg.

To read the pressure value in Pascals, the liquid pressure formula can be used

$$P_{Hg} = \rho_{Hg} g h$$

Inserting h = 76 cm in the equation produces a value of 1 atm in Pascals;

$$P_0 = \rho_{Hg} g h = \left(13\,595\ \frac{kg}{m^3}\right)\left(9.807\ \frac{N}{kg}\right)0.76\ m$$
$$P \approx 101\,325\ Pa$$

This is the correct value for 1 atm expressed in Pascals, however, generally it is easy to remember the approximate conversion 1 atm ≈ 100 000 Pa.

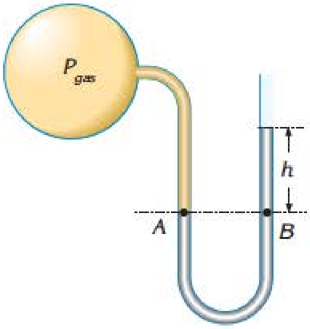


Figure 1.17 The open tube manometer

The open tube manometer is shown in Figure 1.17. It is used to measure the pressure of a gas trapped in a closed container. The pressure at points A and B must be equal, as the points are at the same level and connected with a liquid (the mercury). Point A, is the pressure of the gas inside the balloon; point B is the pressure applied by the mercury column *and* the atmosphere acting over the mercury column. Thus

$$P_A = P_B$$

$$P_{gas} = P_0 + P_{Hg}$$

If, for example the open air pressure is 76 cm-Hg and the height of the mercury column on the right is measured to be h=10 cm, then the pressure of the gas inside the balloon is 86 cm-Hg.

In this example, the pressure reading of the open-tube manometer (i.e. 10 cm-Hg) is called the gauge pressure of the gas. 86 cm-Hg is the absolute pressure of the gas.

Gauge pressure is the difference between absolute pressure and atmospheric pressure. If the absolute pressure of a gas is greater than the atmospheric pressure, the gauge pressure can be expressed as

Gauge pressure = Absolute pressure – Atmospheric pressure

Many pressure measuring devices read the gauge pressure. In other words they are calibrated to read zero, when the pressure of the gas equals atmospheric pressure. Suppose car tyres are inflated until a manometer they are connected to reads 2 atm. The absolute pressure of the air inside the tyres is actually 3 atm, assuming 1 atm open air pressure.

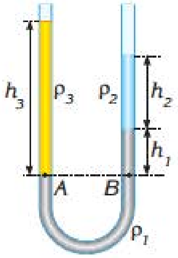


Figure 1.18 The U-tube

For the **U-tube** shown in Figure 1.18, the pressure at points A and B are equal. Since both arms are open to atmospheric pressure, it cancels out on both sides of the equation. Thus, the equation becomes

$$\rho_3 g h_3 = \rho_1 g h_1 + \rho_2 g h_2$$

1.3 ARCHIMEDES' PRINCIPLE

The magnitude of the lifting force applied by a liquid upon an object was first formulated by Archimedes.

Archimedes' Principle: The apparent loss in weight of a body immersed in a fluid is equal to the weight of the displaced fluid.

Figure 1.19, shows that the lifting force of the water on the object equals the weight of the overflowing water.

$$F_b = \text{Weight of displaced liquid}$$

$$F_b = m_{\text{displaced liquid}}\, g$$

$$F_b = \rho_{\text{liquid}} V_{\text{displaced liquid}}\, g$$

Since the volume of overflowing liquid equals the volume of the object under the liquid surface (called the 'immersed volume'), the formula can be written for the magnitude of the force trying to lift the object upwards. This is called the 'buoyant force', and it can be represented as follows:

$$F_{\text{buoyant}} = \rho_{\text{liquid}} V_{\text{immersed}}\, g$$

The lifting (buoyant) force of water and other liquids is a direct result of the dependence of liquid pressure on depth. Consider the cylindrical object, completely immersed in a liquid, as shown in Figure 1.20. The liquid applies a net force on the object, directed upwards, because the upward liquid pressure under the object, is greater than the downward liquid pressure, over the object. The force caused by the pressure difference is the buoyant force of the liquid.

We can verify the buoyant force formula using pressure difference

$$F_{\text{net}} = F_{\text{up}} - F_{\text{down}}$$

$$F_{\text{net}} = P_2A - P_1A = (P_2 - P_1)\, A$$

$$F_{\text{net}} = (\,\rho_{\text{liq}} g h_2 - \rho_{\text{liq}} g h_1)\, A$$

$$F_{\text{net}} = \; g(h_2 - h_1)\, A$$

$$F_{\text{net}} = \rho_{\text{liq}} g\, L\, A$$

Where, L × A is the volume of the object in the liquid. Thus, we can write;

$$F_{\text{buoyant}} = \rho_{\text{liq}} V_{\text{immersed}}\, g$$

This is the same formula as derived above.

This formula is the upward force trying to lift an object, immersed in a liquid. Whether the object sinks or floats depends upon its weight, W.

Think about an object completely immersed in a liquid, as shown in Figure 1.21. If $W > F_b$, the object will sink, if $W = F_b$, the object remains in the same position, and finally if $W < F_b$, the object rises upwards, to float.

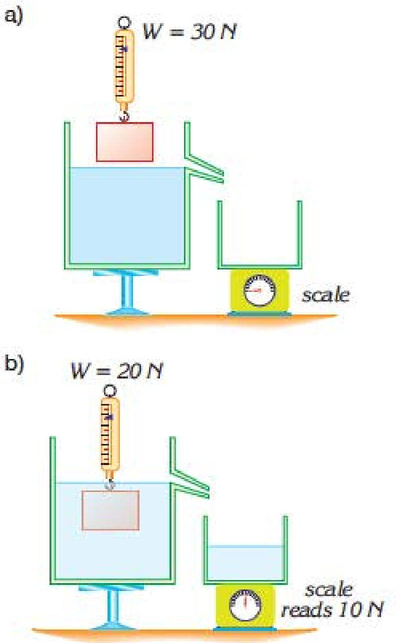


Figure 1.19 The weight loss of the object equals the weight of displaced water

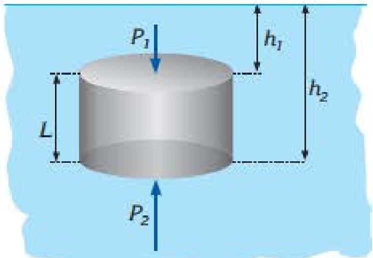


Figure 1.20 The difference in pressure acting on the object leads to a net force upwards

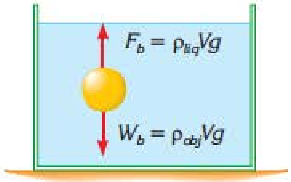


Figure 1.21 $V_{\text{immersed}} = V_{\text{object}}$, since the object is completely under water. Will it float or sink?

The floating condition can be expressed in terms of the densities of the object and liquid, in which it is immersed. The buoyant force has its greatest value when the object is completely immersed under water. If this maximum value of buoyant force cannot lift the object, the object will sink.

Now consider an object completely under water ($V_{immersed} = V_{object}$). If the buoyant force equals the weight of the object, the object stays in the same position. Starting from the condition for remaining in the same position

$$\text{Weight} = F_{buoyant}$$

$$m_{object}\, g = \rho_{liquid}\, V_{immersed}\, g$$

$$\rho_{object}\, V_{object} = \rho_{liquid}\, V_{imersed}$$

$$\rho_{object} = \rho_{liquid}$$

For an object completely immersed in water, the condition, weight = $F_{buoyant}$ means $\rho_{object} = \rho_{liquid}$.

Thus

If $\rho_{object} < \rho_{liquid}$ then the object floats in the liquid.

If $\rho_{object} = \rho_{liquid}$ then the object stays where it is left, totally immersed in the liquid.

If $\rho_{object} > \rho_{liquid}$ then the object sinks to the bottom of the liquid.

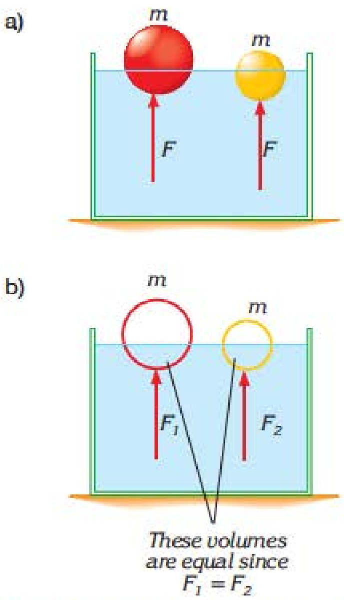


Figure 1.22 Two objects made of different materials floating on water.

Floating Objects

The two spheres in Figure 1.22 are made of different materials, such as wood and cork. The spheres both float in the same liquid and have the same mass. On which sphere does the water act with a greater force?

The question above does not have anything to do with Archimedes' principle. It is a simple equilibrium problem. Since both objects have the same weight, and both of them stay on the water's surface, without the aid of any external force (the only forces acting on the sphere are the lifting force of the water and the object's weight), the buoyant force of water on both spheres must be equal.

In addition, both spheres must have the same volume under the water surface, since the magnitude of the buoyant force is proportional to the immersed volume of an object, These findings can be summarised as follows:

'Floating' means 'weight = buoyant force'

It is possible to justify Archimedes' principle using a different approach:

In Figure 1.23, the 'section A' of water was 'carrying' the 'section B' of water before the object took its place. Section A continues to apply the same force on the object, as it occupies the same volume. If the object is floating on water, its weight equals the weight of the displaced water.

If it sinks, on the other hand, the weight of the object exceeds the weight of the water occupying the same volume as the object.

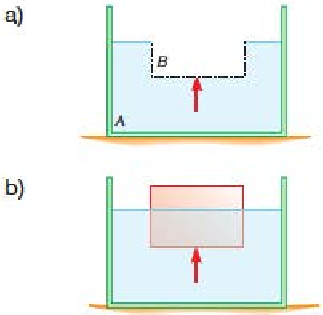


Figure 1.23 The weight of displaced water equals the weight of the object, if the object floats

Example 1.4 Weight loss in water

An object weighs 120 000 N in air and 80 000 N (when completely immersed) in water as shown in Figure 1.24. What is the density of the object?

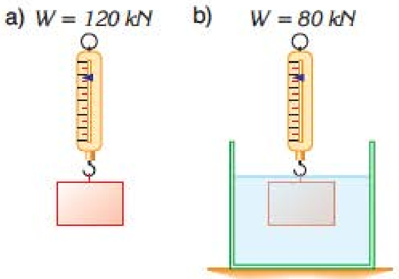


Figure 1.24 40 kN of water is displaced

Solution

The object loses 40 000 N when it is fully immersed in water.

The forces acting on the object are shown in Figure 1.25.

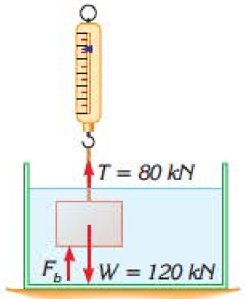


Figure 1.25 The upthrust of water upon the object can be calculated using the equilibrium condition

The object is in equilibrium.

$$F_{up} = F_{down}$$

$$F_{buoyant} + 80\ 000\ \text{N} = 120\ 000\ \text{N}$$

$$F_{buoyant} = 40\ 000\ \text{N}$$

Having found the magnitude of the buoyant force from the equilibrium condition, we can now use Archimedes' principle:

$$F_{buoyant} = \rho_{liquid} V_{immersed}\, g$$

$$V_{immersed} = \frac{F_{buoyant}}{\rho_{liquid}\, g}$$

$$V_{immersed} = \frac{(40\ 000\ \text{N})}{(1000\ \text{kg/m}^3)(10\ \text{N/kg})}$$

$$V_{immersed} = V_{object} = 4\ \text{m}^3.$$

$$\rho = \frac{m}{V} = \frac{12000\ \text{kg}}{4\text{m}^3}$$

$$\rho = 3000\ \text{kg/m}^3$$

Example 1.5 Immersion ratio

What percent of the total volume of a piece of ice will float on the surface of water? Density of ice and water are 900 kg/m^3 and 1000 kg/m^3, respectively.

Solution

Figure 1.26 shows the forces acting on the piece of ice. The weight of ice and the buoyant force are the only two forces acting.

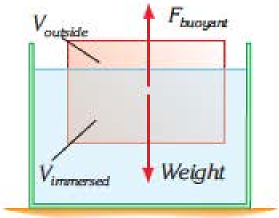


Figure 1.26 The two forces acting upon the floating ice

Since there are no other forces and since the object is in equilibrium;

$$F_{buoyant} = \text{Weight}$$

$$\rho_{liquid} V_{immersed}\, g = \rho_{object} V_{object}\, g$$

$$\frac{V_{immersed}}{V_{object}} = \frac{\rho_{object}}{\rho_{liquid}}$$

This ratio holds not only for this problem, but for all objects floating in a liquid. Substituting the numerical values

$$\frac{V_{\text{immersed}}}{V_{\text{ice}}}=\frac{900\ \text{kg/m}^3}{1000\ \text{kg/m}^3}=0.9$$

90% of the volume of the ice is immersed in water. Therefore 10% must be floating above the water's surface. Figure 1.27 is helpful in remembering the relationship between 'density ratio' and 'immersion ratio'.

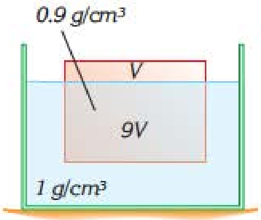


Figure 1.27 The immersion ratio for ice

1.4 FLUID MECHANICS

Fluid mechanics is the branch of physics related to flowing fluids. The motion of a liquid can take quite complicated forms, sometimes making fluid mechanics one of the most complicated branches of physics. For the simple case of an incompressible liquid, flowing in a non-turbulent way, we have two very useful equations.

Consider a liquid flowing parallel to the sides of a pipe of varying cross-section, as shown in Figure 1.28.

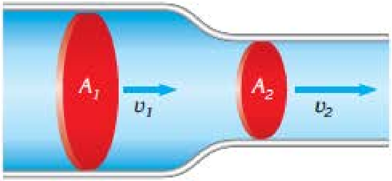


Figure 1.28 Speed increases with decreasing cross-sectional area

The liquid flows faster when the area becomes smaller. The product of speed and cross sectional area of the flow is constant along the pipe. Thus

$$A_1\times v_1=A_2\times v_2$$

The equality above is called the **equation of continuity**.

The equation of continuity is a direct result of the conservation of mass.

The dimensions of the product, (area) × (velocity), is the volume of liquid flowing past a point in unit time: $\left[\text{m}^2\times\frac{\text{m}}{\text{s}}\right]=\left[\frac{\text{m}^3}{\text{s}}\right]\Rightarrow\left[\frac{\text{volume}}{\text{time}}\right]$.

The equation of continuity holds for all incompressible fluids. 'Incompressible' means that the volume of the fluid does not decrease when squeezed externally, thus its density doesn't decrease under increasing external pressure. All liquids are practically incompressible. (All substances are compressible to some degree, but for liquids and most solids, the volume change is negligible.)

Example 1.6 Mass flow rate

Derive a formula for the mass flow rate (mass flow per unit time) of a fluid flowing through a pipe of cross-sectional area A, and velocity v.

Solution

Figure 1.29 shows a liquid undergoing a displacement of Δx in a time Δt, as it flows along the tube. The liquid volume ΔV passing through a cross section during this time interval is shaded in the figure.

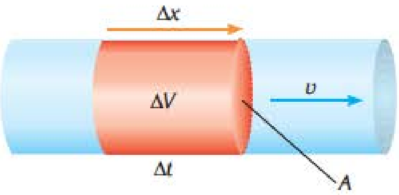


Figure 1.29 The volume DV passes through area A in time Dt.

The mass contained in volume ΔV flows past the area, A in unit time.

$$\begin{pmatrix}\text{Mass flow in}\\ \text{unit time}\end{pmatrix} = (\text{density}) \times \begin{pmatrix}\text{Volume passing}\\ \text{in unit time}\end{pmatrix}$$

If we express **mass flow rate** as Δm/Δt, we can write;

$$\frac{\Delta m}{\Delta t} = \rho \times \frac{\Delta V}{\Delta t}$$

$$\frac{\Delta m}{\Delta t} = \rho \times \frac{A \times \Delta x}{\Delta t} = \rho \times A \times \left(\frac{\Delta x}{\Delta t}\right)$$

$$\frac{\Delta m}{\Delta t} = \rho A v$$

analysing the units,

$$\frac{kg}{s} = \frac{kg}{m^3} \times m^2 \times \frac{m}{s}$$

We see that, the amount of mass passing through a cross section perpendicular to the direction of a current is given by

$$\begin{pmatrix}\text{Mass flow in}\\ \text{unit time}\end{pmatrix} = (\text{density}) \times (\text{area}) \times (\text{speed})$$

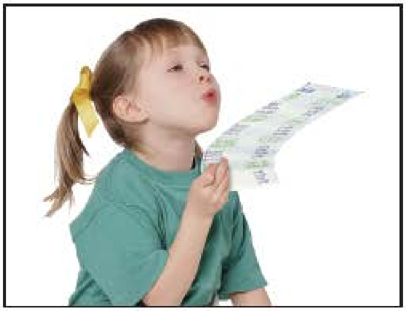


Figure 1.30 Faster air, above the sheet of paper, causes a lower pressure above the sheet of paper thus, the paper rises.

Now we know the reason why the product (Area) × (velocity) is a constant along a length of liquid in a pipe. It is because mass is conserved; the same mass of a liquid must flow in unit time through all cross-sections along a pipe. This requires (Δm/Δt) to be constant along the flow.

Bernoulli's Equation

The pressure-depth relationship, $P = \rho g h$, holds only for stationary liquids. A liquid can have different pressures at two points of the same depth, if it is flowing at different speeds at these points.

The pressure of a fluid decreases with increasing speed. This principle is easy to demonstrate, as shown in Figures 1.30 and is known as 'Bernoulli's principle'. It has many practical applications. The force lifting an airplane arises from the difference in pressures incident on the upper and lower surfaces of the plane's wings. Figure 1.31 shows the cross-section of an airplane wing. The curved upper surface makes the air flow faster above the wing. This is because an air molecule travelling along the greater upper surface moves a longer distance in the same time that an air molecule travels the shorter under-wing distance.

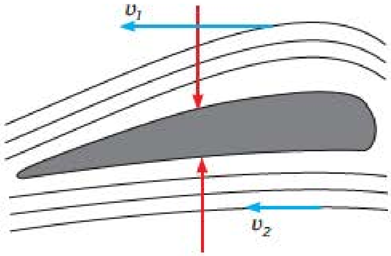


Figure 1.31 A speed difference produces an upward net force on the wing

To find the quantitative relationship between fluid speed and pressure, the conservation of energy principle is used. Consider a pipe of varying cross-section, as shown in Figure 1.32. When the piston on the left moves for a distance Δx_1, the piston on the right moves a distance Δx_2. The masses of the liquids in the shaded regions must be equal;

$$\Delta m_1 = \Delta m_2$$

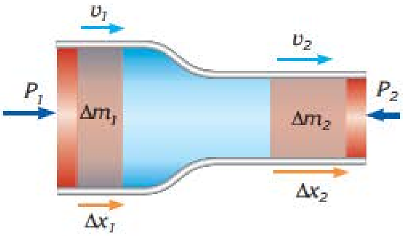


Figure 1.32 Bernoulli's equation is a direct application of the conservation of energy

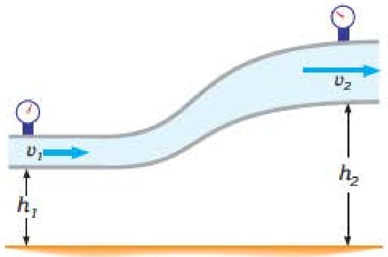


Figure 1.33 A pipe of varying cross-section and height

Neglecting the mass of the pistons;
Net work done (on the liquid between the pistons) = Net energy increase (of the liquid)

$$F_1\Delta x_1 - F_2\Delta x_2 = \frac{1}{2}\Delta m_2 v_2^2 - \frac{1}{2}\Delta m_1 v_1^2$$

$$(P_1A_1)\Delta x_1 - (P_2A_2)\Delta x_2 = \frac{1}{2}(\rho A_2\Delta x_2)v_2^2 - \frac{1}{2}(\rho A_1\Delta x_1)v_1^2$$

$$P_1A_1\Delta x_1 + \frac{1}{2}(\rho A_1\Delta x_1)v_1^2 = P_2A_2\Delta x_2 + \frac{1}{2}(\rho A_2\Delta x_2)v_2^2$$

However, $A_1\Delta x_1 = A_2\Delta x_2$. Cancelling this from both sides of the equation gives

$$P_1 + \frac{1}{2}\rho v_1^2 = P_2 + \frac{1}{2}\rho v_2^2$$

If the height of the liquid is also changing over the length, as shown in Figure 1.33 the potential energy change must be included in the derivation. The result given below is known as **Bernoulli's equation**:

$$P_1 + \frac{1}{2}\rho v_1^2 + \rho g h_1 = P_2 + \frac{1}{2}\rho v_2^2 + \rho g h_2$$

Example 1.7 The speed of water

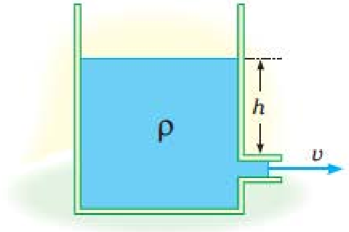


Figure 1.34 What factors affect the speed of water?

Water flows through a small hole on the side of an aquarium, as shown in Figure 1.34. Find the speed with which water pours out of the hole.

Solution

The two cross sections must be determined in order to apply Bernoulli's principle. A_1 and A_2 are shown in Figure 1.35.

Since the liquid is open to atmospheric pressure on both sides, Bernoulli's equation becomes

$$P_o + \frac{1}{2}\rho v_1^2 + \rho g h_1 = P_o + \frac{1}{2}\rho v_2^2 + \rho g h_2$$

v_1 is very small compared to v_2, since $A_1 >> A_2$.

Setting $v_1 \approx 0$ we obtain;

$$\frac{1}{2}\rho v_2^2 = \rho g(h_2 - h_1)$$

$$v_2^2 = 2gh$$

$$v_2 = \sqrt{2gh}$$

which is a ubiquitous expression.

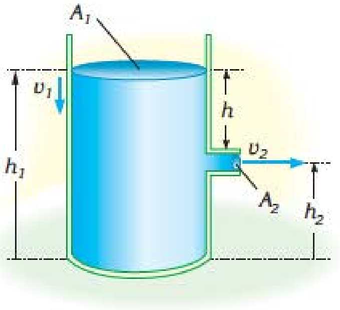


Figure 1.35 The parameters of flowing water.

Summary

Definitions

Density is mass per unit volume:

$$\rho = \frac{m}{V} \qquad \text{unit}: \frac{kg}{m^3}$$

Pressure is (perpendicular) force per unit area:

$$P \equiv \frac{F}{A} \qquad \text{unit}: Pa \equiv \frac{N}{m^2}$$

Laws and Principles

Pascal's principle: Liquids transmit pressure equally in all directions

Formulas

Stationary liquid pressure:

$$P_{liquid} = \rho g h$$

Buoyant force:

$$F = \rho_{liquid} V_{immersed}\, g$$

Equation of continuity:

$$A_1 v_1 = A_2 v_2$$

Mass flow rate:

$$\frac{\Delta m}{\Delta t} = \rho v A$$

Bernoulli's Equation:

$$P_1 + \frac{1}{2}\rho v_1^2 + \rho g h_1 = P_2 + \frac{1}{2}\rho v_2^2 + \rho g h_2$$

QUESTIONS AND PROBLEMS

(Take $\rho_{water}=1000$ kg/m^3, $\rho_{mercury}=13\,600$ kg/m^3, $g=10$ N/kg, 1 atm = 100 kPa)

1.1 Density

1. The density of 1 kg of iron is 7.9 g/cm^3. What is the density of 2 kg of iron?

2. Is density an intrinsic or bulk property of matter?

3. Convert 5 lt into dm^3 and m^3.

4. Express 0.048 lt in dm^3 and m^3

5. Convert 0.8 kg/lt into g/dm^3.

6. What is the volume of 1 kg of aluminum in cm^3? (Take $\rho_{Aluminum}$ = 2.7 g/cm^3)

7. What is the mass of 750 liters of gasoline? (Take $\rho_{gasoline}$ = 680 kg/m^3)

8. Water and ethyl alcohol are mixed in equal volumes. What is the density of the mixture? (Take $\rho_{alcohol}$ = 800 kg/m^3)

9. Show that when two liquids of equal mass are mixed, the density of the mixture is given by $\rho_{mixture} = \dfrac{2\rho_1\rho_2}{\rho_1+\rho_2}$ where ρ_1 and ρ_2 are the densities of the liquids.

1.2 Pressure

10. What is the definition of pressure?

11. What is the SI unit for pressure?

12. Convert 0.3 Pa into N/cm^2.

13. Express 12 000 N/m^2 in atm.

14. Express 70 cm-Hg in atmospheres and in Pascals.

15. What are the factors affecting the atmospheric pressure?

16. An 85-kg man stands on his skis each having an area of 0.2 m^2. What is the pressure applied by the pair of skis on the snow in units of Pascals (Pa)?

17. What is the pressure applied by an iron cube on the floor? The side length of the cube is 10cm. (Take ρ_{iron}=7.9 g/cm^3)

18. What is the difference between transmission of force by solids and by liquids?

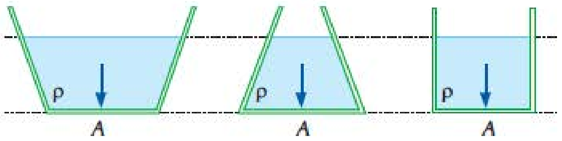
19. At what depth below a lake surface is the total pressure 3 times the normal atmospheric pressure?

20. A pressure of 10^6 Pa of hot steam applies 100 kN force to a surface. What is the area of the surface in m^2?

21. A test-tube is plugged with a cork and heated. The pressure of the air inside reaches 200 kPa. What is the pressure force pushing the cork from inside, if the cross-sectional area is 1 cm^2?

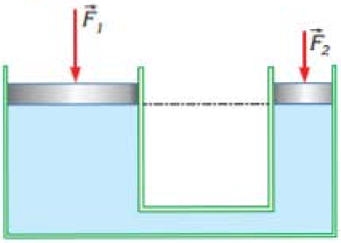
22. A swimming pool has dimensions 30 m × 10 m and a flat bottom. When the pool is filled to a depth of 3 m with water, what is the pressure force exerted by the water (a) at the bottom? (b) on the larger side?

23.



Three containers having different shapes, but equal base areas are filled with the same liquid up to the same height. Compare the pressures and the pressure forces applied by the liquids on the bottoms of the containers.

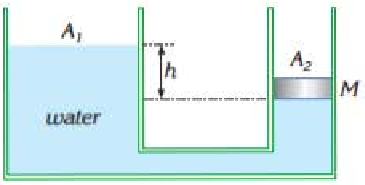
24.



The area of the larger piston of the hydraulic lever in the figure is 10 times the area of the smaller piston. What is the force acting on the larger piston, if the force on the smaller piston is 1 800 N? The pistons are weightless.

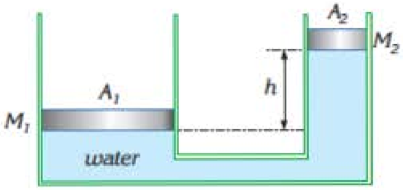
25. The hydraulic lever in the previous question is filled with oil. Does the answer to the previous question change if water is used in place of oil?
(Take $\rho_{water} > \rho_{oil}$)

26.



The cross-sectional areas of the two arms of the hydraulic lever are $A_1=100$ cm^2 and $A_2=10$ cm^2, and the mass of the piston is M = 4 kg. What is the height, h, in units of cm, when the system is at rest as shown in the figure?

27.

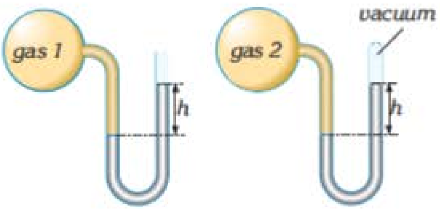


The cross-sectional areas of the two arms of the hydraulic lever are $A_1=100$ cm^2 and $A_2=$ 10 cm^2 and the masses of the pistons are $M_1=4$ kg, $M_2=0.2$ kg, respectively. What is the height h, in units of cm, when the system is at rest, as shown in the figure?

28. The pressure of 1 mm-Hg is called 1 torr. Express 1 torr in Pa.

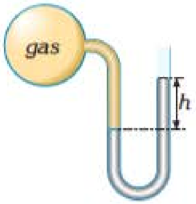
29. Differentiate between gauge pressure and absolute pressure.

30.



Two manometers are shown in the figure. In which barometer does the height of the mercury column equal the absolute pressure of the gas in the balloon? Which one reads the gauge pressure?

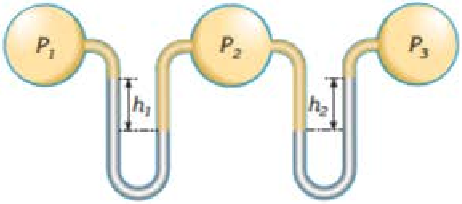
31. An open-tube mercury barometer is shown in the figure. What is the absolute pressure of the gas in the balloon if h=20 cm? Atmospheric pressure is $P_0=1$ Atm. Express the answer:



a) In cm-Hg

b) In atm

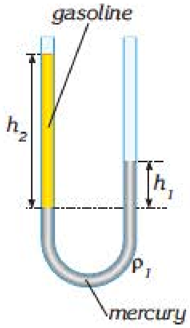
32.



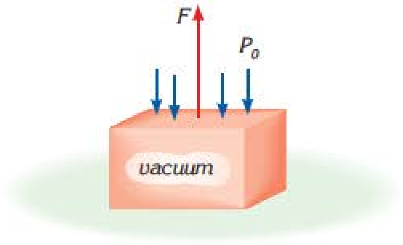
What is the value of pressure P_3, cm-Hg in, if $h_1=23$ cm, $h_2=15$ cm and $P_1=1$ Atm? The liquid in the tubes is mercury.

33. The diameter of one arm of a U-tube is three times the diameter of the other arm. Some mercury is poured into the larger arm. What is the ratio of the heights of the mercury columns in the two arms?

34. Gasoline is poured into the left arm of a U-tube, which already has some mercury in it. When the gasoline column reaches a height of $h_2 = 19.4$ cm, the level difference between the mercury surfaces becomes $h_1 = 1$ cm. What is the density of the gasoline? The density of mercury is 13.6 g/cm^3.



35.



The bottom of a rectangular box is removed. The box is placed on the floor and the air inside is evacuated. What force is needed to lift the box from the floor? The base area of the box is 100 cm^2. Air pressure is 100 kPa.

1.3 Archimedes' Principle

36. An object of volume of 0.06 m^3 is completely immersed in water. What is the buoyant force acting on the object?

37. The buoyant force acting on an object, completely immersed in a liquid, is 1.8 N. What is the density of the liquid, if the volume of the object is 225 cm^3?

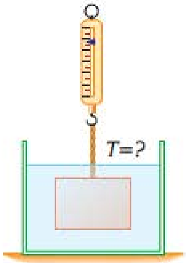
38. What is the buoyant force acting on a ship travelling with 900 m^3 of its volume under water?

39. The buoyant force acting on an object, completely under water is 800 N. What is the buoyant force acting on the same object when it is completely immersed in oil, of density 800 kg/m^3?

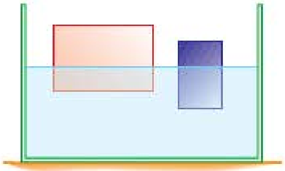
40. The weight of an iron block is 790 N. What is the apparent weight of the same block when it is completely immersed in water? The density of iron is 7 900 kg/m^3.

41. An objects weighs 18 000 N in air and 15 000 N when completely immersed in water. What is the density of the object?

42. The object in the figure is made of a material of density 3000 kg/m^3. What is the tension in the rope, which suspends the object, when it is completely immersed in water. The mass of the object is 200 kg.



43.



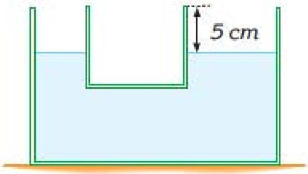
Two blocks of equal mass float in the water, as shown in the figure. The blocks are made of different materials. Upon which block is the buoyant force greater?

44. What is the weight of a ship travelling with 900 m^3 of its volume under water?

45. A wooden block floats over water with 0.08 m^3 of its volume under the surface of the water. What is the mass of the block? (Take $\rho_{wood} = 600$ kg/m^3)

46. A large wooden block having a weight of 62 000 N floats over water. The density of wood is 620 kg/m^3. What additional force is needed to completely sink the block, such that it is totally under water?

47.

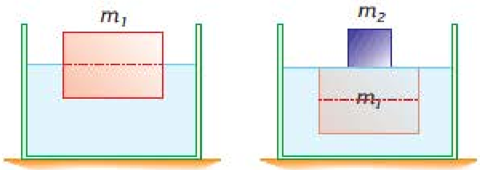


An open box with a base area of 400 cm^2 floats over water with 5 cm of its height floating over the surface of the water, as in the figure. What additional mass can this box carry without sinking?

48. A large wooden block of mass 1800 kg is partially floating on the water. What is the volume of a block of wood which floats on the surface of the water? The density of wood is 600 kg/m^3.

49. A raft of surface area 5 m^2 floats on the surface of the water. A 100-kg man jumps onto the raft. By how many centimetres does the raft sink due to the man's additional weight?

50.



A plastic block of mass m_1 partially floats over the water surface, with half of its volume under the water surface. The plastic block sinks completely when an iron cube of mass m_2 is placed on top of it, as shown in the figure. What is the ratio of the two masses, m_2/m_1?

51. A large ship floats in a small lake. Does the level of water in the lake rise or fall if the ship sinks?

1.4 Fluid Mechanics

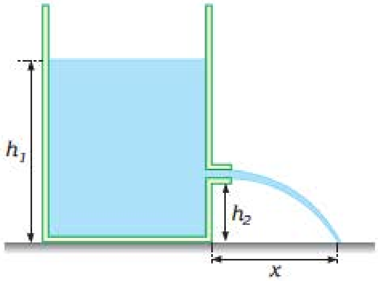
52. Water flows through a pipe of varying cylindrical cross-section. The speed of the water is 4 m/s when the pipe radius is 3 cm. What is the speed of water through a cross-section of 6 cm radius?

53. The speed of an incompressible fluid increases as the cross-sectional area of the pipe through which it is flowing decreases. By what factor does the diameter of the pipe decrease for an increase in flow speed by a factor of 4?

54. Water comes out of a tap at a speed of 1 m/s. The cross-sectional area of the water exit is 2 cm^2. How many kilograms of water is wasted when the tap is accidentally left on for 1 hour?

55. Explain why the water stream from a kitchen tap gets narrower as water flows downward.

56.



Water flows out of a small opening on the side of a container at a height h_2=5 cm from the floor, as shown in the figure. At what horizontal distance from the container does the water jet fall on the floor, when the water level in the container is h_1=50 cm, measured from the floor?

CHAPTER

2

Structure of Matter

The physical world reaching our consciousness, through our five senses, is composed of matter and electromagnetic waves. Electromagnetic waves consist of oscillating electric and magnetic fields. Matter is made up of atoms. Historically the idea of the 'atom' stems from the question of whether a substance is infinitely divisible, or eventually a 'smallest part' which you cannot divide anymore is reached. Today it is known that an atom is itself composed of even smaller particles and is divisible. The atom is continuing to reveal secrets about its own internal structure via high technology. To explain the behaviour of a gas we can use a simplistic model, in which, atom scan be treated as simplistic billiard balls, flying around and colliding with each other.

2.1 ELEMENTS AND COMPOUNDS

There are 92 kinds of naturally existing elements. Iron, copper, hydrogen and oxygen are all examples of elements. An element is a substance which cannot be separated into simpler substances. If a piece of iron, is divided into two, then again into two, and so on, at the end an iron *atom* will remain. An iron atom is still iron. It has all the properties of the element iron. If it is divided from this point onwards, however, and the iron atom is split into its parts, the element iron is no longer present.

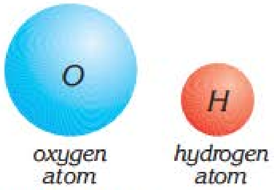


Figure 2.1 An atom is the smallest part of an element

An **atom** is the smallest part of an element, which has the chemical properties of the element (Figure 2.1).

Since there are 92 kinds of naturally occurring elements, there must be 92 different kinds of naturally existing atoms. Surrounding us, however, are millions of different kinds of substances. Where do these all come from?

The answer to this question is that, most of the substances surrounding us are *compounds*. Water, for example is a compound. There are no water atoms. If we take a piece of ice, divide it into two, then again into two, and so on, at the end we will be left with a water *molecule*. A molecule can be a combination of two or more atoms. A water molecule for example, consists of one oxygen and two hydrogen atoms, as shown in Figure 2.2. If we separate a water molecule into its constituent atoms, we do not have the substance, water anymore.

The smallest part of a substance, which has the chemical properties of the substance is a **molecule**.

It is impossible to imagine how small an atom is. If an atom was magnified so as to make it as large as an apple, on the same scale, an apple would be as large as the Earth.

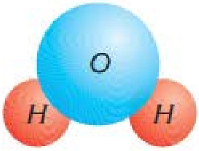


Figure 2.2 A water molecule

If all 6 billion people on Earth were given the task of counting the number of atoms on a pinhead, it would take 100 years to complete the task, each person counting 10 atoms per second.

The structure of an atom, as portrayed by the classical theory resembles the structure of the solar system. All atoms consist of a nucleus in the centre and electrons revolving around the nucleus, as shown in Figure 2.3. The nucleus contains 99.9 percent of the mass of an atom, however it is concentrated in only 10^{-15} of the volume of the atom. Inside the atom nearly all of the space is empty. The radius of an atom is approximately 100 000 times the radius of its nucleus.

The nucleus itself is composed of protons and neutrons. The mass of a proton is approximately equal to the mass of a neutron, but a proton is 1836 times heavier than an electron*.

Protons are positively charged and neutrons are neutral (uncharged), so the nucleus is positively charged. Electrons on the other hand, are negatively charged. The charge of an electron exactly equals the charge of a proton in magnitude. Therefore, for an atom to be electrically neutral, the number of electrons must be equal to the number of protons, as shown in Figure 2.4.

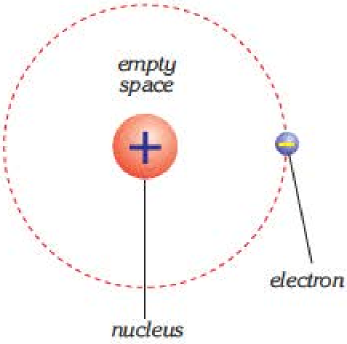


Figure 2.3 The structure of an atom

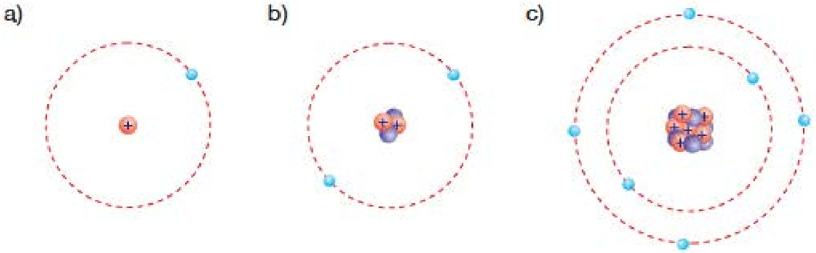


Figure 2.4 The number of electrons equals the number of protons in a neutral atom a) Hydrogen b) Helium c) Carbon

Atoms can donate or accept electrons. When an atom donates electrons it becomes positively charged. Accepting electrons from an external source makes an atom negatively charged.

Two or more atoms can combine by transferring or sharing electrons. Such combinations of atoms are called molecules, as was discussed above. Figure 2.5 shows three molecules of familiar substances. The electrical force which keeps the atoms together as a molecule is called a **chemical bond**. The formation or disintegration of molecules is called a chemical reaction. A **chemical reaction** is a process in which an atom either transfers or starts to share one or more electrons.

Protons are never transferred between atoms. The number of protons in the nucleus is called the **atomic number** of an element and is represented by Z. It is the main characteristic of a chemical element. Chemical properties of an element are determined by its atomic number. Atomic number is an index by which we can name elements..

If an atom has 26 protons for example, it is an iron atom. Different types of iron

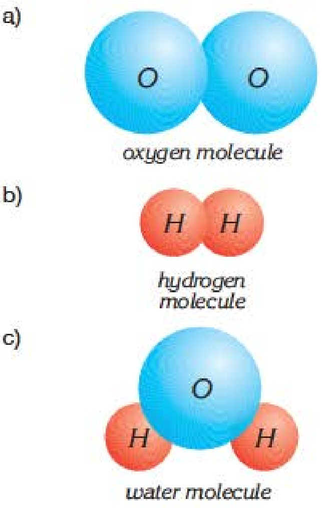


Figure 2.5 Molecules of oxygen, hydrogen and water.

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* $m_{proton} = 1.673 \times 10^{-27}$ kg, $m_{neutron} = 1.675 \times 10^{-27}$ kg, $m_{electron} = 9.11 \times 10^{-31}$ kg

atoms can have different numbers of neutrons. Each of two or more atoms with the same atomic number, but with a different number of neutrons is called an **isotope**. Isotopes of iron for example can have 30, 31 or 32 neutrons, but all of them must have 26 protons to be recognised as 'iron'. Isotopes of iron have the same chemical properties, but naturally, physical properties (like mass) are different.

Atomic mass number is the sum of the number of neutrons and protons. Atomic mass number is denoted by A. If we represent the number of neutrons by N, we can write

$$A = N + Z$$

Atomic mass number and atomic number of an element is displayed on the left upper and left lower corners, respectively, of the symbol of the element.

$$^{\text{atomic mass number}}_{\text{atomic number}}X \Rightarrow {}^{A}_{Z}X$$

for any element X.

As an example, the symbol of carbon is C. The carbon atom has 6 protons. Suppose an isotope of carbon has 6 neutrons and another isotope has 8 neutrons. We represent these two isotopes by

$${}^{12}_{6}C \quad \text{and} \quad {}^{14}_{6}C$$

The units gram or kilogram are not suitable for expressing the mass of an atom, as it is too small. Instead, a different unit of mass, called the **atomic mass unit** (u) is used.

$$1\text{u} \equiv \frac{\text{mass of a single } \left({}^{12}_{6}C\right) \text{carbon atom}}{12} = 1.66 \times 10^{-27}\,\text{kg}$$

Since the mass of electrons can be neglected, compared to the mass of protons or neutrons, the mass of an atom, expressed in u, and the atomic mass number of that atom are approximately equal.

Mass of ${}^{(1)}_{1}H = 1.0078$ u, mass of ${}^{(4)}_{2}He = 4.0026$ u, mass of ${}^{(12)}_{6}C = 12.0000$ u, mass of ${}^{(14)}_{7}N = 14.0031$ u

2.2 THE CONCEPT OF THE MOLE

A dozen eggs means 12 eggs, a dozen apples means 12 apples, a dozen atoms means 12 atoms.

Similarly, 1 mole of a substance is 602 000 000 000 000 000 000 000 ($= 6.02 \times 10^{23}$) particles of that substance.

1 mole of eggs means 6.02×10^{23} eggs, 1 mole of apples means 6.02×10^{23} apples, 1 mole of oxygen atoms means 6.02×10^{23} oxygen atoms. The number 6.02×10^{23} is known as Avogadro's number and is denoted by N_A.

$$N_A = 6.02 \times 10^{23}$$

The mass of 1 mole of an element expressed in grams, numerically equals the mass of one atom of that element expressed in u's.

1 mole of carbon ($^{12}_{6}C$) atoms is 12.0000 grams, 1 mole of hydrogen ($^{1}_{1}H$) atoms is 1.0078 grams (≈1g), 1 mole of helium ($^{4}_{2}He$) atoms is 4.0026 grams (≈4 g), 1 mole of nitrogen ($^{14}_{7}N$) atoms is 14.0031 grams (≈14 g)...

Atoms of some elements in gaseous form prefer to stay as atoms, while some others form molecules. Helium gas for example, consists of helium atoms. Nitrogen gas on the other hand, consists of nitrogen molecules. Thus, a particle of helium gas refers to an 'atom' of helium, whereas a particle of nitrogen refers to a 'molecule' of nitrogen (or a group of two nitrogen atoms). Figure 2.6 shows these two gases.

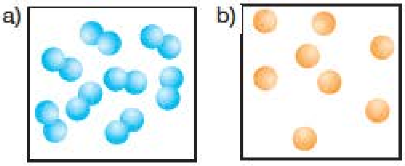


Figure 2.6 a) 8 particles of b) 8 particles of helium gas nitrogen gas

1 mole of any gas contains $N_A = 6.02 \times 10^{23}$ particles. These particles can be either atoms or molecules (groups of atoms), according to the nature of the gas.

The number of moles in a given amount of substance proves to be a very important physical quantity. In many formulas the amount of matter must be expressed in moles, instead of grams or kilograms. We can calculate the number of moles using the following fomulas:

$$n = \frac{m}{M} \qquad \text{and} \qquad n = \frac{N}{N_A}$$

n = number of moles

M = mass of one mole (molar mass)

m = mass of given amount of substance

N = number of particles (atoms or molecules) in a given amount of substance

N_A = Avogadro's number

Exercise 2.1 Number of molecules

How many water molecules are there in 3.6 kg of water? (Molar mass of water, $M_{H_2O} = 18$ g/mole)

Solution

First find how many moles of water molecules there are in 3.6 kg water.

Given $m = 3.6$ kg

$M = 18$ g/mole $= 0.018$ kg/mole

$$n = \frac{m}{M} = \frac{3.6\ \text{kg}}{0.0018\ \text{kg/mole}}$$

$n = 200$ moles

Now the number of molecules can be found

$N = nN_A$

$N = 200\ \text{moles} \times 6.02 \times 10^{23}$ molecules/mole

$N = 1.2 \times 10^{26}$ water molecules.

We found 1.2×10^{26} molecules in 3600 g water. This means 3.3×10^{22} molecules in 1 g.

2.3 THE MOLECULAR NATURE OF MATTER

There are three basic assumptions in molecular - kinetic theory

- All matter consists of small particles
- The particles are in ceaseless irregular motion
- The particles interact with each other

Careful observation gives us hints about the molecular nature of matter. Diffusion in liquids and gases for example, is best explained in terms of molecular motion. A drop of ink allowed to fall into water is distributed throughout the whole volume of water in a short time, even if the water is not externally stirred. A similar phenomenon can be observed when perfume is sprayed in one corner of a room. The odour will quickly reach all other corners of the room, due to the invisible motion of air molecules, even though the air in the room appears to be perfectly still.

It is possible to estimate the size of a molecule by means of a simple experiment. The experiment was first carried out by Benjamin Franklin. Allow a droplet of oil to fall onto the surface of a still water surface. One drop of volume 1 mm^3 will spread over the surface area of the water, which is approximately a 0.6 m^2. We can assume that the oil forms a layer only 1 molecule thick, as shown in Figure 2.7.

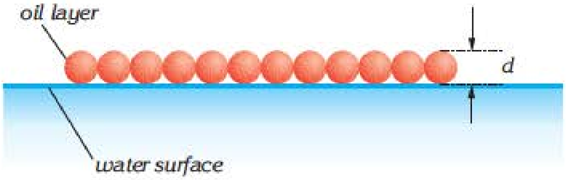


Figure 2.7 Oil spreads evenly over the water's surface

Since (volume = base area × height), we can write

$$\text{thickness} = \frac{\text{volume}}{\text{area}} \Rightarrow d = \frac{1\,\text{mm}^3}{0.6\,\text{m}^2} = \frac{0.001\,\text{cm}^3}{6000\,\text{cm}^2} \approx 1.7 \times 10^{-7}\text{cm}$$

This number obtained by Franklin in the 18th century gives us an idea about the size of a molecule of the oil used in the experiment. Since organic compounds contain many atoms in their molecules, the size of an atom is even smaller than the size of an oil molecule.

Today's value for the order of magnitude of the **diameter of an atom** is about 10^{-8} cm. In other words, 100 million atoms side by side is 1 cm long.

The idea of all matter consisting of discrete particles dates back to ancient Greece. In the 17th century, Newton explained the expansion of a gas in terms of the motion of molecules.

Ludwig Boltzmann and later J. C. Maxwell developed the kinetic theory of gases in the second half of the 19th century. The kinetic theory was able to explain the macroscopic properties of gases (such as pressure or temperature) in terms of the motions and interactions of particles forming the gas. However, the theory was based on the assumption of the existence of such particles (molecules) interacting in clearly defined ways. Direct evidence for the existence of atoms was missing. Lack of evidence hampered a wide scale acceptance of the theory among the scientific community of that time.

The first direct evidence for the molecular nature of matter came from Einstein's mathematical explanation of Brownian motion in terms of the motion of water molecules in 1905, winning him the Nobel Prize.

Brownian motion is the random movement of pollen grains (about 0.001 mm in diameter) suspended in water. It was first observed by botanist Robert Brown in 1827. The motion is visible under a microscope and is completely random, as shown in Figure 2.8.

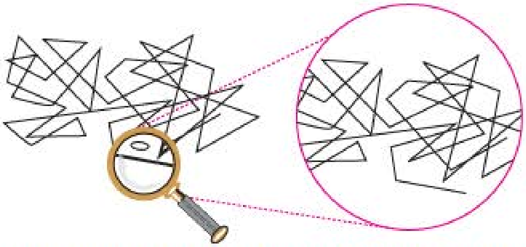


Figure 2.8 Zoom into the pattern of a particle's motion many times; you will observe a similar pattern.

At first the ceaseless motion had been attributed to organic causes. Then it was observed that pollen grains, that had been stored for a century were also moving in the same way.

Another observation is that Brownian motion is more rapid for smaller particles. These small particles zigzag around clearly in space, while larger particles are agitated, but remain in the same position.

Brownian motion was caused by invisible water molecules, randomly moving in all directions, and striking the pollen grains suspended in the liquid, as shown in Figure 2.9.

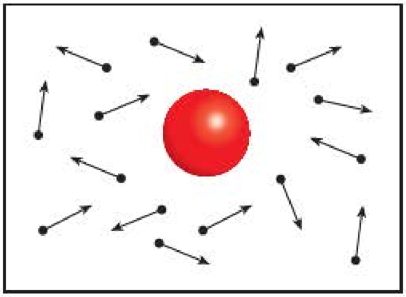


Figure 2.9 Brownian motion is caused by the random motion of air molecules

Brownian motion is a good example of the 'statistical fluctuation' phenomenon. Billions of molecules continuously strike the pollen grain from all sides. When the number of particles is so large, the motion is random, and the impulse received in opposite directions would normally, on average, cancel out. However, at a given instant, the impulse received in a given direction can exceed the impulse received in the opposite direction. As a result the grain of pollen has a net impulse and is pushed randomly around.

2.4 THE NATURE OF INTERMOLECULAR FORCES

Potential Energy

If there is an attractive or repulsive force within a system consisting of two bodies, we can assign a potential energy to the system, only if the force is conservative. The 'two bodies' under consideration can be two planets or two molecules; the force between them can be electrical or gravitational.

If two bodies attract each other, the potential energy of the system is negative.

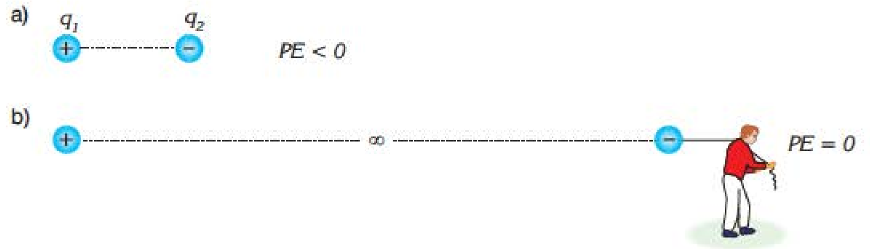


Figure 2.10 a) The system has potential energy b) Potential energy of the system increases to zero as one of the charges is pulled to infinity. So the potential energy must have been negative at the beginning.

Considering a system of two particles, which attract each other, as shown in Figure 2.10. Suppose one particle is fixed in place, and the other is removed by an external force.

When the distance between the particles becomes very large, the particles do not 'see' each other any more. We can say the potential energy is zero in this case.

However, the external force did work on the system by removing one of the particles, giving energy to the system. The two particle system receives energy from an external force, and its potential energy becomes zero. Therefore the initial energy of the system must have been negative.

Consider two objects electrically attracting each other. One of them is fixed in position and the other is given an initial velocity, hence kinetic energy, as shown in Figure 2.11. Kinetic energy is always a positive quantity. Potential energy due to an attractive force is negative. Two possibilities can be examined:

a) The magnitude of the potential energy of the system is greater than the magnitude of the kinetic energy, as shown in Figure 2.11.a. Total energy is negative. the second object does not have enough kinetic energy to break free, it will return, so the particles are 'bound together'.

b) The magnitude of the potential energy of a system is smaller than the magnitude of the kinetic energy. Total energy is positive. The second object can escape and does not return. The objects are 'free', as shown in Figure 2.11.b.

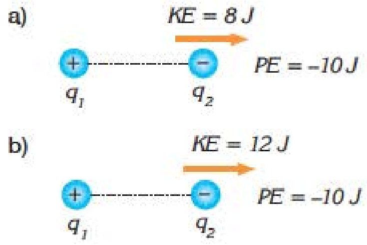


Figure 2.11 a) A bound system b) An unbound system

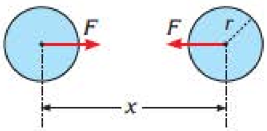
Intermolecular Forces

Forces of attraction and repulsion act between molecules of a substance. These forces are of electrical origin.

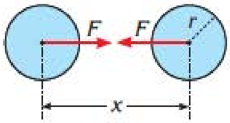
A molecule is electrically neutral, but the positive and negative charges in the molecule are not distributed homogeneously over the molecule's volume. The nuclei of atoms constitute 'lumps' of positive charge, the electrons around the nucleus form 'clouds' of negative charge. The configuration becomes even more complicated when atoms combine to form a molecule. As a result, each molecule has a unique electric charge distribution.

The exact nature of the interaction between two molecules depends on the size and structure of molecules. Thus, it is not possible to represent an expression relating the force or potential energy between any two molecules. However, it is possible to describe the general characteristics of intermolecular forces.

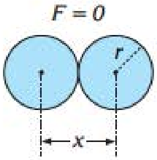
Let us simplify the case by assuming the molecules are spherical;



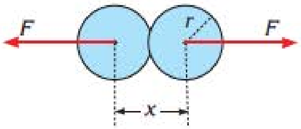
When the distance between the centres of molecules is greater than the sum of the molecules' radii, the net force between them is attractive. (Point A in Figure 2.12)



If molecules get closer, attraction increases. (Between A and B in Figure 2.12)



The attractive force suddenly decreases, if molecules continue to approach, and drops to zero when the distance between the molecular centres equals the sum of their radii. (Between B and C in Figure 2.12)



The molecules start to repel each other strongly, as the electron clouds x start to overlap. (Point D in Figure 2.12)

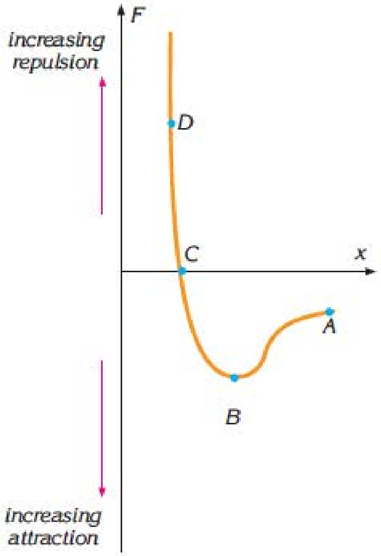


Figure 2.12 The force between two molecules.

The nature of intermolecular forces in solids and liquids can be observed by trying to compress any solid object and trying to compress water in a closed container. It is clear that the strength of the repulsive forces between the molecules is very great. The tendency of separate water drops on a surface, towards combining to form one large drop, is caused by the attractive force between liquid molecules. 'Wetting' of a liquid can also be explained in terms of the intermolecular forces between liquid molecules and the molecules of the wetted substance.

2.5 STATES OF MATTER

Matter is found in four states: Solid, liquid, gas and plasma. We are familiar with the first three states, although 99.9% of the matter in the universe (not on Earth) is in the plasma state. The hot interiors of stars contain matter in the plasma state. Solid, liquid and gas states are possible only at low temperatures.

Solids: Molecules of a solid are bound to each other by spring-like forces as described above, and as shown in Figure 2.13. Molecules in the solid structure are not stationary, but they oscillate about their equilibrium positions. The binding potential energy of a solid molecule is greater in magnitude than its kinetic energy. These bonds between molecules give the solid its definite shape and volume.

In a solid: average kinetic energy of molecules < |average potential energy of molecules|

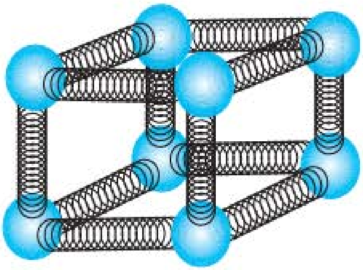


Figure 2.13 A model of a solid

Liquids: When the solid substance is heated, its temperature rises. A higher temperature means molecules in the solid structure have higher kinetic energies. As the temperature rises, the average kinetic energy of molecules approximately equals their average potential energy. Thus, a molecule is free to leave its place in the structure. On the other hand, the molecule does not have enough kinetic energy to escape and leave the substance. Thus, the molecule escaping one location in the molecular structure of the substance, is trapped in another location for a short time. The substance not able to preserve its shape anymore and, it begins to flow. This is the liquid state of matter.

In a liquid, a molecule jumps from one local arrangement of molecules to another. Since the average spacing between the molecules of a liquid is nearly equal to the spacing between solid molecules, a state change from solid to liquid does not increase the volume of the substance very much.

In a liquid: Average. kinetic energy of molecules ≈ |Average potential energy of molecules|

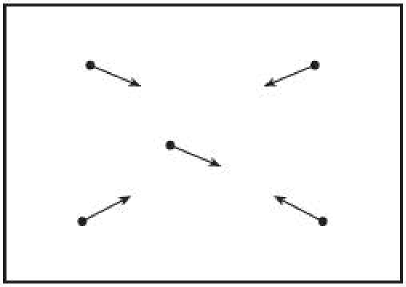


Figure 2.14 A model the gas state

Gases: Increasing the temperature of a liquid causes its molecules to move even faster, increasing the kinetic energies of the molecules. When molecules in the liquid state have enough kinetic energy to break free from the intermolecular bonds, they escape, and the substance transforms into a gas state.

In a gas: Average kinetic energy of the molecules >> |Average potential energy of the molecules|

Therefore, molecules of a substance in the gaseous state are not bound to each other. They are free to move around, occupying all the available volume, as shown in Figure 2.14. Matter in the gas state has neither a definite shape nor a definite volume.

2.6 AN IDEAL GAS

A gas is said to be 'ideal' if it has the following properties:

a) The average distance between gas particles is large compared to the size of the particles. This means a gas occupies volume because of the motion of its particles; the size of the particles is negligible. The volume of an ideal gas drops to nearly zero as it is compressed.

b) The potential energy between gas molecules is negligible, compared to the average kinetic energy of molecules. This means that the potential energy of interaction between molecules can be taken as zero. Thus, molecules of an ideal gas have only kinetic energy.

Neglecting potential energy between molecules, means assuming zero attractive force between the molecules. In other words, the molecules of an ideal gas do not 'see' each other from a distance until they collide.

c) Molecules of an ideal gas undergo 'elastic collisions' with one another and with the walls of the container. This means total kinetic energy before and after the collision are the same. The total kinetic energy of the particles remains constant for an isolated system.

To summarise, the particles of an ideal gas behave like billiard balls flying around in a steel-walled room.

Which gases are ideal, which gases are not? The answer is that no gas is ideal. Molecules of all gases more or less interact with each other, giving rise to intermolecular potential energies, and no gas is compressible to zero volume. However, nearly all gases can be treated as ideal gases at low densities. Later the behaviour of real gases will be discussed.

2.7 DISTRIBUTION OF MOLECULAR SPEEDS

Particles of a gas fly around randomly, colliding with each other and with the walls of the container. As we assumed for an ideal gas, collisions are elastic, conserving the total kinetic energy. However, the kinetic energy of a particle changes during each collision, as its speed increases or decreases. A particle typically undergoes about 1 000 000 000 collisions in one second, under normal conditions, and each collision makes the molecule totally forget about its motion before the collision.

Naturally, it is neither possible, nor necessary, to determine the speed of each molecule in a gas sample. Speed (or kinetic energy) of a single molecule changes every instant, however, the average value of the kinetic energy of all molecules in a gas sample does not change in time. Later it will be seen that macroscopic quantities, such as temperature or pressure, depend on the average value of the kinetic energy of the gas molecules.

Most of the molecules of a gas move at intermediate speeds. Molecules that are too fast or too slow molecules constitute a small minority. The graph in Figure 2.15 shows the distribution of molecular speeds for a gas at a given temperature.

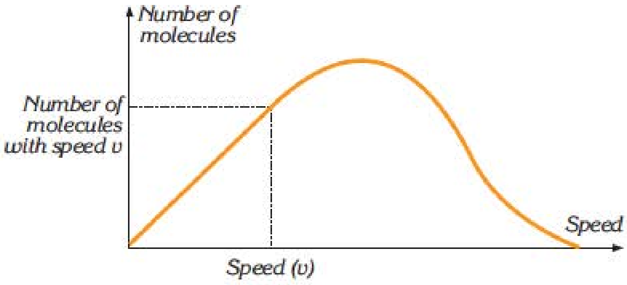


Figure 2.15 The distribution of molecular speeds

In the graph of Figure 2.15, the horizontal axis represents the speed of the molecules; the vertical axis represents the number of molecules having a given speed.

Since it is not possible to determine the exact number of molecules in a gas sample with a definite speed v, the vertical axis actually represents the number of molecules with speeds near v (between v and v + Δv).

At higher temperatures, molecules become faster, on average, so that the fraction of molecules with higher speeds increases. This fact can be seen in Figure 2.16. This explains why most chemical reactions are faster at higher temperatures. When two molecules collide faster, the probability of a reaction occurring between them is higher. Increasing the temperature quickly increases the number of molecules fast enough to react chemically.

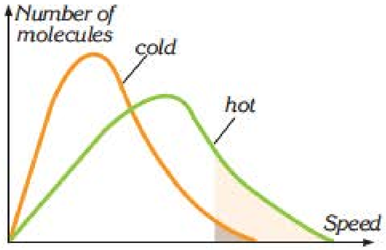


Figure 2.16 The effect of temperature on the molecular distribution of speeds. The shaded regions are the fraction of molecules with speeds above a given value

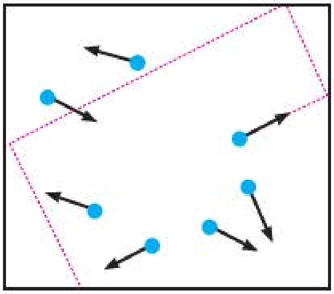


Figure 2.17 The pressure is caused by the bombardment of gas molecules

2.8 THE PRESSURE OF A GAS

Pressure applied by a solid or a liquid is caused by its weight. The pressure of a gas is caused by the motion of its molecules.

For a gas sample, in a closed container, pressure applied by the gas on the walls of the container is caused by the gas molecules bombarding the walls. This is shown in Figure 2.17. Since the force exerted by each molecule is very small, and billions of impacts take place every instant, it is impossible to feel or measure the contribution of a single molecule. The net force on a wall is the sum of the forces exerted by all molecules.

The pressure of a gas depends upon two factors:

- The speed (or kinetic energy) of the molecules striking a wall of the container: Striking faster means applying more force.
- The number of molecules striking unit area of a wall every instant: More molecules means more force.

The exact relationship between the number of molecules, the kinetic energy of the molecules and the pressure of a gas will be discussed in chapter 6.

Summary

Definitions

An **atom** is the smallest particle of an element, having the chemical properties of the element.

The smallest particle of a substance, having the properties of the substance, is called a **molecule**. A molecule can have two or more atoms.

The number of protons in the nucleus is called the **atomic number** of an element.

Atomic mass number is the sum of the number of neutrons and the number of the number of protons.

Atomic mass unit (u)

$$1\ \text{u} = \frac{\text{mass of a single } \left({}^{12}_{6}\text{C}\right) \text{ carbon atom}}{12}$$

1 **mole** of a substance represents 6.02×10^{23} particles of that substance.

Laws and Principles

The mass of 1 mole of an element expressed in grams, approximately equals the atomic mass number of that element.

Formulas

The number of moles

$$n = \frac{\text{total mass}}{\text{mass of 1 mole}} = \frac{m}{M}$$

$$n = \frac{\text{total number of particles}}{\text{number of particles in 1 mole}} = \frac{N}{N_A}$$

QUESTIONS AND PROBLEMS

(Take $N_A = 6 \times 10^{23}$)

2.1 Elements and Compounds

1. What are the three main types of particles in an atom?
2. How does the mass of a proton compare with the mass of an electron?
3. How does the charge of a proton compare with the charge of an electron?
4. What is the difference between atomic number and atomic mass number?
5. What is the relationship between atomic mass and atomic mass number?
6. What information about an atom is needed to identify an atom?
7. What is an isotope?

2.2 The Concept of the Mole

8. What is the mass of 7 moles of hydrogen gas? (Take $M_{H_2} = 2$ g/mole)
9. How many hydrogen molecules do 7 moles of hydrogen contain?
10. How many hydrogen atoms do 7 moles of hydrogen gas contain? Molecules of hydrogen gas consist of two hydrogen atoms.
11. The mass of 12×10^{23} molecules of carbon monoxide is 56 g. What is the molar mass of carbon monoxide?
12. The molar mass of CO_2 is 0.044 kg/mole. What is the mass of a single carbon dioxide molecule?
13. What is the total mass of 18×10^{23} molecules of helium gas? (Take $M_{He} = 4$ g/mole)
14. Which contains a greater number of molecules, a glass of water or a glass of mercury?
    (Take $\rho_{Hg} = 13.6$ g/cm^3, $\rho_{H_2O} = 1$ g/cm^3, $M_{Hg} = 200.5$ g/mole, $M_{H_2O} = 18$ g/mole)
15. A gas sample occupying a volume of 0.5 m^3, contains 1.2×10^{25} molecules. The density of the gas is 1.28 kg/m^3. What is the molar mass of the gas?

2.3 The Molecular Nature of Matter

16. What are the three basic assumptions of molecular-kinetic theory?
17. What is Brownian motion?
18. Why is Brownian motion less observable for larger particles?

2.4 The Nature of Intermolecular Forces

19. Do two molecules normally pull or push each other? Does this question have a simple answer?
20. Give examples of everyday observations which give us hints about the nature of forces the between molecules.

2.5 States of Matter

21. How do the magnitudes of the kinetic and potential energies of molecules of a gas compare?
22. Which states of matter are incompressible? Why?
23. In which state of matter do the molecules have the highest total energy?

2.6 An Ideal Gas

24. Under what conditions can we consider a gas to be ideal?
25. Which gases are ideal?

2.7 Distribution of Molecular Speeds

26. Do all the molecules of a hot gas move faster than all the molecules of a cold gas?
27. Why do most chemical reactions occur more rapidly at higher temperatures?

2.8 The Pressure of a Gas

28. What is the difference between gas pressure and liquid pressure, from a molecular point of view?
29. Why does the pressure of a gas increase with increasing temperature, from a molecular point of view?

Temperature and Gas Laws

CHAPTER 3

We can feel the difference between a hot object and a cold object. We may say that temperature is the degree of hotness of an object. However, this definition is intuitive and makes reference to our personal sense of touch. To assign a numerical value to temperature, a quantitative approach must be employed. A cup of tea can be 'warm' according to one person and 'very hot' according to another. Objective methods are necessary to measure the numerical value of temperature.

A device used to measure temperature is called a 'thermometer'. There are numerous types of thermometers, utilising different physics laws, as their working principle. It is possible to measure temperature using many principles of physics: the resistance of a wire, the expansion properties of solids, even infrared radiation. The most common thermometer, which we are all familiar with, utilises the expansion of a liquid along a narrow glass tube as its measurement principle.

3.1 TEMPERATURE SCALES

The mercury thermometer was invented by G. D. Fahrenheit in 1714. It consists of a thin glass tube sealed at both ends (capillary tube) partly filled with mercury. Figure 3.1 shows such a thermometer. Above the mercury column is a vacuum, for the mercury to expand freely. As the temperature increases the mercury column in the tubes rises. Assigning numerical values to different heights of the mercury column is called 'calibrating the thermometer'. Using different criteria for calibration gives rise to different temperature scales.

The two most commonly used temperature scales in daily life are the Celsius and Fahrenheit scales.

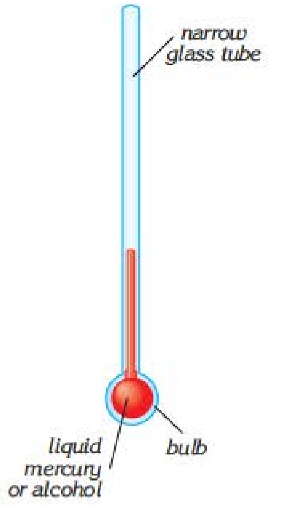


Figure 3.1 A Mercury thermometer

Swedish astronomer Celsius used the freezing and boiling points of water, under 1 atm pressure, as the reference points for his scale. The temperature of an ice-water mixture is taken as 0 °C and the temperature of boiling water is taken as 100 °C* on the Celsius scale. The height between these two reference points is divided into 100 equal parts. This is why the Celsius scale is also called the centigrade (=100 grades) scale.

In scientific studies the Kelvin scale is used to express temperature. The Kelvin scale is also called the 'absolute temperature scale'. Later in this chapter more will be learnt about the Kelvin scale.

The relationship between the three temperature scales is shown in Figure 3.2.

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* 100 °C is pronounced 100 degrees Celsius. 100 K, on the other hand, is pronounced 100 Kelvin, the word degrees is not used.

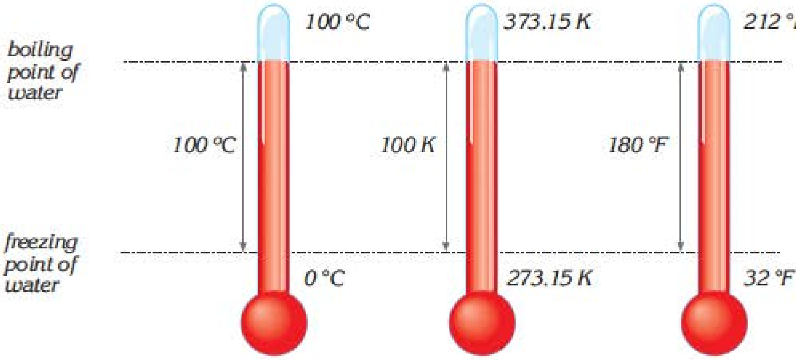


Figure 3.2 A comparison of the three temperature scales

In between the freezing and boiling points of water, the temperature increases from 0 to 100 on the Celsius scale, and from 273.15 to 373.15 on the Kelvin scale and from 32 to 212 on the Fahrenheit scale. Consequently, the conversion formulas must be

$$T_K = T_C + 273.15 \quad \text{and} \quad \frac{T_C}{100} = \frac{T_F - 32}{180}$$

There is a problem with one of the physical properties of the capillary tube thermometer. Two capillary thermometers, calibrated in the same way, give different temperature readings if the liquids used in the thermometers are different. Suppose the freezing and boiling points of water are marked on a mercury thermometer and a glycerine thermometer. The two thermometers agree at the fixed points, of 0 °C and 100 °C, but they show different values for intermediate temperatures. This effect is caused by the different expansion properties of each liquid.

To overcome this difficulty and reach universal agreement on the full range of the temperature scale, a 'constant volume gas thermometer' is used. This thermometer is also used in defining the Kelvin scale. The structure of constant volume gas thermometer will be examined at the end of this chapter.

Example 3.1 Changes in temperature

A metal casserole dish is heated from 20°C to 110°C. What is the temperature change on the Celsius and Kelvin scales?

Solution

As usual

(Change) = (Final) - (Initial)

$$\Delta T = T_f - T_i$$

In Celsius

ΔT (in °C) = 110 °C – 20 °C

ΔT (in °C) = 90 °C

First express the initial and final values in Kelvins.

$$T_K = T_C + 273.15$$

$$110\ °C = 383.15\ K$$

$$20\ °C = 293.15\ K$$

The temperature change becomes

$$\Delta T\ (\text{in K}) = 383.15\ K - 293.15\ K$$

$$\Delta T\ (\text{in K}) = 90\ K$$

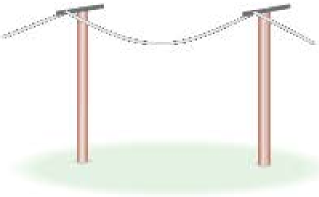
Therefore

$$\Delta T(\text{in } °C) = \Delta T\ (\text{in K})$$

Although the initial and final values are different on the two scales, the numerical values of the changes are equal.

3.2 THERMAL EXPANSION

All substances, solid, liquids, and gases, expand (undergo an increase in their size) with increasing temperature. Power lines sagging in the summer and tightening in the winter are common observations, as shown in Figure 3.3.


summer

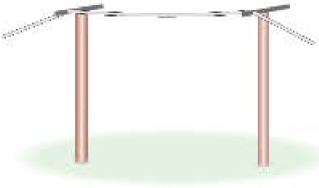

winter

Figure 3.3 The expansion of power cables

Three types of expansions will be investigated: Linear, area and volume expansions.

Linear Expansion

For long, thin objects, like a long copper wire, a change in thickness is very small and can be neglected. Thus, we can assume the object is one dimensional, and the expansion is linear.

Change in length depends on three factors:

- ➤ Change in temperature (ΔT)
- ➤ Initial length (L_0)
- ➤ The substance from which the object is made (α)

α is called the 'linear expansion coefficient' and is different for each material.

Consider the thin long steel rod in Figure 3.4.

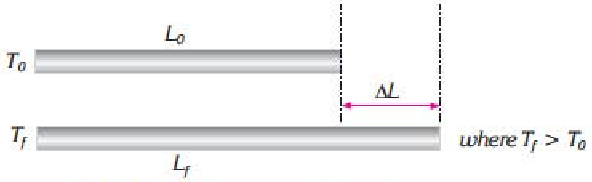


Figure 3.4 Linear expansion of a rod

Material	α (1/ °C)
Steel	12×10^{-6}
Aluminum	24×10^{-6}
Lead	29×10^{-6}
Glass	9×10^{-6}

Table 3.1 Linear expansion coefficients of various materials

The **linear expansion coefficient** is defined as the fractional change in length $\left(\dfrac{\Delta L}{L_0}\right)$ per unit temperature change (ΔT):

$$\alpha = \frac{\Delta L}{L_0 \Delta T} \qquad \text{The unit of } \alpha \text{ is } \left[\frac{1}{°C}\right]$$

Change in length is given by

$$\Delta L = \Delta L_0 \Delta T^{*}$$

$$L_f - L_0 = \Delta L_0 \Delta T$$

$$L_f = L_0 + \Delta L_0 \Delta T$$

$$L_f = L_0 (1 + \alpha \, \Delta T)$$

When heated, the object expands as a whole, as shown in Figure 3.5.

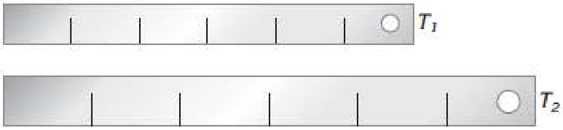


Figure 3.5 Every point on an object expands in all directions. The hole also expands with the length.

It is important to understand that the change in length depends on the initial length. Suppose a 100 cm iron stick expands to (100 + 1) cm when it is heated. In proportion, a 200 cm iron stick will become (200 + 2) cm when it is heated by the same amount. Each half of it gets longer by 1 cm.

Area Expansion

Consider the thin, flat piece of metal shown in Figure 3.6. Suppose the area of the object increases from A_0 to A_f, as temperature increases from T_0 to T_f.

As usual, temperature change is $T = T_f - T_0$ and area change is $A = A_f - A_0$.

The dependence of area change on temperature change is given by

$$\Delta A = 2\alpha A_0 \Delta T$$

The coefficient, α in the formula is the linear expansion coefficient for the material used for the linear expansion formula.

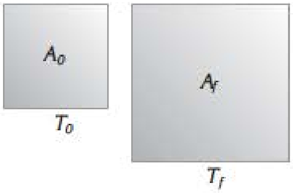


Figure 3.6 Expansion of an area

Volume Expansion

For the three- dimensional object shown in Figure 3.7, the expansion becomes

$$\Delta V = 3\alpha V_0 \Delta T$$

The coefficient, α in the formula is the linear expansion coefficient for the material used in the linear expansion formula.

Since a liquid cannot expand linearly, a linear expansion coefficient (α) is not defined for a liquid.

For liquids, a specific volume expansion coefficient (β) is defined. The expansion formula for a liquid is:

$$\Delta V = \beta V_0 \Delta T$$

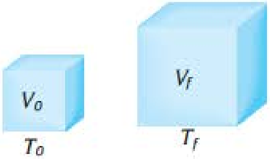


Figure 3.7 Expansion of a volume

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* This formula is not exact. Experiments show that α itself is not constant and changes with temperature.

Example 3.2

The sound of a train

The familiar sound of a moving train is caused by the gaps left between the tracks. If the tracks building the railway were placed in touch with each other, they would buckle on hot days.

Suppose the length of a railroad track is 30 m on a day when the temperature is –10 °C. What is the length of the track at 40 °C? (Take $\alpha = 11\times10^{-6}$ 1/°C)

Solution

$$T = T_f - T_i$$

$$T = 40\ °C - (-10\ °C)$$

$$T = 50\ °C$$

$$\Delta L = \alpha L_0 \Delta T$$

$$\Delta L = \left(11\times10^{-6}\frac{1}{°C}\right)(30\,\mathrm{m})(50\,°C)$$

$$\Delta L = 0.0165\ \mathrm{m} = 1.65\ \mathrm{cm}$$

The track gets longer by 1.65 cm, so the final length is

$$L_f = L_0 + \Delta L$$

$$L_f = 30\ \mathrm{m} + 0.0165\ \mathrm{m}$$

$$L_f = 30.0165\ \mathrm{m}$$

Question

Can we derive the area expansion formula from the linear expansion formula?

Answer

Consider a flat, rectangular metal sheet having sides a and b, as shown in Figure 3.8.a.

When it is heated, the rectangle expands in both dimensions as shown in Figure 3.8.b.

The change in area is:

$$\Delta A = a\Delta b + b\Delta a + \Delta a\Delta b$$

The term $\Delta a\Delta b$ is the product of two changes, so it is negligibly small compared to other terms. We can write

$$\Delta A \approx a\Delta b + b\Delta a$$

Substituting in the expressions for linear changes

$$\Delta a = \alpha a\Delta T \quad \text{and} \quad \Delta b = \alpha b\Delta T$$

The area expression becomes;

$$\Delta A \approx a\Delta b + b\Delta a$$

$$\Delta A \approx a(\alpha b\Delta T) + b(\alpha a\Delta T)$$

$$\Delta A \approx 2\alpha(ab)\Delta T$$

since $ab = A_1$

the area change is

$$\Delta A \approx 2\alpha A_1 \Delta T$$

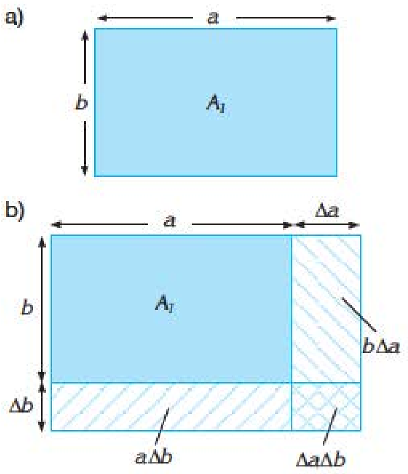


Figure 3.8 Planar objects expand in two dimensions

3.3 MOLECULAR INTERPRETATION OF TEMPERATURE

Temperature can be defined as degree of hotness. What is the physical difference between a hot object and a cold object, besides that experienced by our sense of touch? In other words, which property of a substance determines its temperature?

Molecular - kinetic theory relates temperature of a substance to the motion of molecules forming the substance. The previous chapter explained that all matter (solids, liquids, gases) consists of unimaginably small molecules. These molecules are in a continuous random state of motion called **thermal motion**. The form of thermal motion depends on the phase of the substance. In a solid, molecules oscillate around fixed positions. In a gas, they fly around freely, continuously colliding with each other.

The temperature of a substance is related to thermal motion of its molecules. In general terms, higher temperature relates to faster moving molecules.

Temperature is then a measure of the average kinetic energy of the molecules of a substance.

Average kinetic energy means the sum of the kinetic energies of molecules divided by the number of molecules. The average kinetic energy of gas molecules is a very small number, since the mass of a molecule is so small. At 20 °C for example, an oxygen molecule in air has about 10^{-20} J of kinetic energy.

As mentioned in chapter 2, molecules of a gas can have a wide range of velocities, and the speed of a molecule changes millions of times in a second, due to collisions with other molecules surrounding it. At a given instant one molecule of a gas sample may nearly be at rest, while another molecule may move with almost the speed of light. Consequently, the kinetic energies of molecules of a gas are quite different. However, the average kinetic energy of molecules gives us an idea about the overall behaviour of a gas sample.

A gas sample at a higher temperature contains molecules with a higher kinetic energy, on average, than a colder sample. However, it is possible to find very fast and very slow molecules in both samples.

Chapter 6 derives the fact that

$$\begin{pmatrix}\text{Average KE of} \\ \text{molecules of a gas}\end{pmatrix} = (\text{a constant}) \times (\text{temperature})$$

3.4 THE GAS LAWS

Gas laws are relationships between the macroscopic parameters of a gas. Pressure, volume, and temperature are macroscopic parameters of a gas. However, a quantity like speed or kinetic energy of a single molecule is a microscopic parameter.

As an aid to understanding the gas laws, and thermodynamics, a 'cylinder - piston' system will be used.

Consider a cylinder - piston system as described in Figure 3.9. The piston is tight fitting enough not to allow any gas to escape, but in the same time, moves up wards and downward without friction.

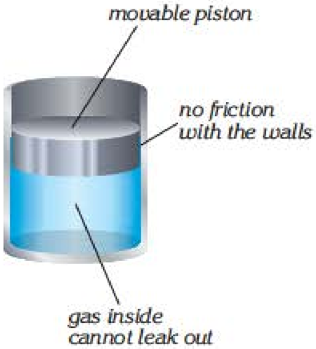


Figure 3.9 A cylinder - piston system

Practically, this is a difficult apparatus to produce, but it is a very useful system as an aid to understanding the basics of the physics of a gas.

The pressure applied to the insides by the piston can be adjusted, by changing the weight of the piston as described below.

Example 3.3 Adjusting pressure using a movable piston

A sample of gas is confined at a cylinder - piston system, as shown in Figure 3.10. The mass of the piston is given as 20 kg and the area of the piston is 50 cm^2. Taking atmospheric pressure as 100 kPa, what is the pressure of the gas inside the cylinder, if the system is in equilibrium?

Solution

Using the equilibrium condition for the piston, to calculate the pressure of the gas inside.

Net force on the piston is zero (Figure 3.10).

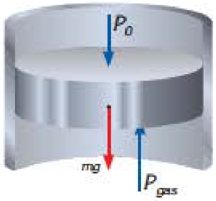


Figure 3.10 The piston is in equilibrium with three forces acting vertically on it.

$$mg + F_{atmosphere} - F_{gas} = 0$$

$$mg + P_0A - P_{gas}A = 0$$

$$P_{gas}A = mg + P_0A$$

$$P_{gas} = \frac{mg}{A} + P_0$$

$$P_{gas} = \frac{(20\ \text{kg})(10\ \text{N/kg})}{\left(50\times10^{-4}\ \text{m}^2\right)} + 100\ \text{kPa}$$

$$P_{gas} = 40\ \text{kPa} + 100\ \text{kPa}$$

$$P_{gas} = 140\ \text{kPa}$$

Question

How can the pressure of the gas inside the cylinder be increased in the previous exercise? Does the pressure increase if the gas is heated?

Answer

Since the pressure of the gas is equal to the total external pressure, we can increase the gas pressure by increasing the weight of the piston. This can be carried out, for example, by placing an additional load on the piston.

What if the gas is heated? Will it apply more pressure?

When temperature increases, the gas tries to apply more pressure. However, since the piston is movable and the atmospheric pressure is constant, even a small increment in the gas pressure moves the piston upwards, increasing the volume. An increase in the volume causes a decrease in the gas pressure, until it is equal to the external pressure once again. Therefore, if the piston is movable, the gas pressure cannot be increased, unless the weight of the piston is changed.

Thus, a movable piston implies a constant pressure in a cylinder - piston system.

Historically, the relationships between temperature, pressure and volume of a gas were established in the 17th century by various scientists. These relationships are remembered by the names of the scientists who discovered them. Three gas laws will be investigated here; under the condition of constant temperature, constant pressure, and constant volume.

The Boyle - Mariotte Law

The pressure - volume relationship of a gas sample at constant temperature.

Changing the volume and pressure of a gas sample at a constant temperature is called an isothermal process.

'Isothermal' means occurring at 'constant temperature'.

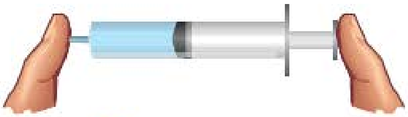


Figure 3.11 Decreasing the volume, causes an increase in pressure

When a fixed amount of gas is compressed, decreasing its volume, its pressure increases. This fact can be observe by trying to squeeze the air in a syringe with its nozzle closed, as shown in Figure 3.11. Pushing the piston requires more and more force as the volume of the air trapped inside decreases. This 'syringe experiment' is not a good example for an isothermal process. As the air in the syringe is compressed, temperature increases. To keep the temperature constant care must be taken.

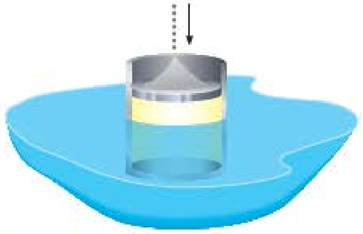


Figure 3.12 How can an isothermal process be achieved?

To realise an isothermal process the following precautions are taken. A cylinder is placed, as shown in Figure 3.12, in a lake (heat reservoir) to keep the temperature constant. In order to increase the pressure slowly, infinitesimally small masses; such as grains of sand, are dropped on the piston, one by one. The impact of each grain pushes the piston down a little and the temperature tries to increase by, say, 0.01 °C, but since we cannot heat the whole lake, and the process is slow enough, the gas inside the cylinder will have time to cool down, until its temperature equals the temperature of the lake water. Thus, the temperature of the gas is kept constant.

The lake, in the process described above is acting as a **heat reservoir**. This means it is cooling down (or heating up) another object, without changing its own temperature.

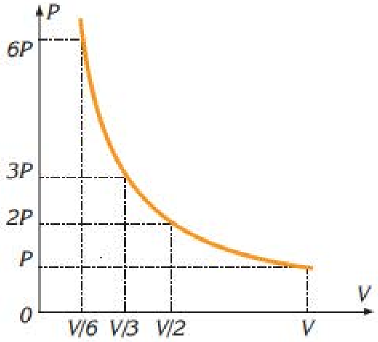


Figure 3.13 An isothermal process

Plotting a graph of pressure versus volume (P-V) of the gas, during an isothermal process, gives a dependence similar to that shown in Figure 3.13.

As seen in the graph, the PV product is constant at constant temperature.

For an ideal gas at constant temperature

$$PV = \text{const}$$

$$P_1V_1 = P_2V_2$$

The curve plotted in the P-V graph of Figure 3.13 is called an isotherm. Along the curve at all points, temperature is constant. If the same experiment is performed at a different constant temperature, a similar curve on the P–V graph can be obtained, as shown in Figure 3.14.

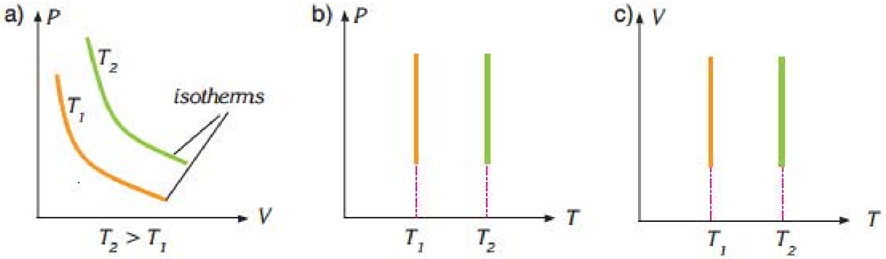


Figure 3.14 Isotherms on different graph plots a) P–V graphs of two isothermal processes, taking place at two different constant temperatures b) Corresponding P–T diagrams c) Corresponding V–T diagrams

Question

Can the pressure-volume relationship be explained at constant temperature, in terms of the motion of molecules?

Answer

Remember that the pressure of a gas depends on two factors in terms of molecular motion.

- The Speed of the molecules striking a walls of the container (average kinetic energy of molecules.)
- Number of molecules striking unit area of a wall in unit time.

Since temperature is constant, the average speed of the molecules does not change during an isothermal process.

However, when the volume is decreased, the number of collisions with the walls in unit time increases.

Consider a 'gas sample' having only one molecule, as shown in Figure 3.15.

When the volume is decreased by half, the time between two successive collisions also decreases by half. Consequently, the number of collisions in unit time doubles, increasing the pressure by a factor of 2.

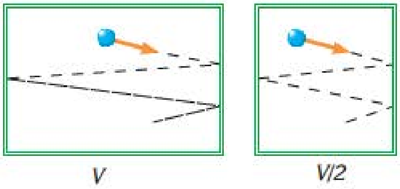


Figure 3.15 A Single molecule gas

The Gay - Lussac Law

The volume – temperature relationship of a gas sample at constant pressure.

Changing the volume and temperature of a gas sample, at constant pressure is called an isobaric process.

'Isobaric' means occurring at 'constant pressure'.

Keeping the pressure of a gas constant is relatively easy. As long as the external pressure on the gas sample is constant, and the gas is in equilibrium with the surroundings, the pressure of the gas is constant.

Consider the cylinder - piston system. If the piston is stationary, or moving with constant velocity, the net force on it is zero. Therefore the pressure of the gas inside, must be equal to the pressure applied upon the gas by the piston.

In the following discussion and examples, assume the piston moves with constant speed.

Suppose an ideal gas sample, confined in a cylinder-piston system, is heated. An increase in volume is observed, as temperature increases, this is shown in Figure 3.16. Conversely, if the gas is cooled, the piston moves downward, as shown in Figure 3.17. Plotting the volume versus temperature (V-T) graph on the Celsius scale for the cooling process, gives a plot similar to Figure 3.18.

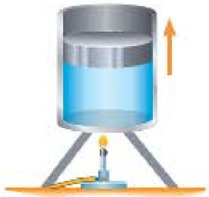


Figure 3.16 Isobaric expansion

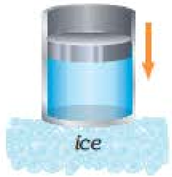


Figure 3.17 An isobaric cooling

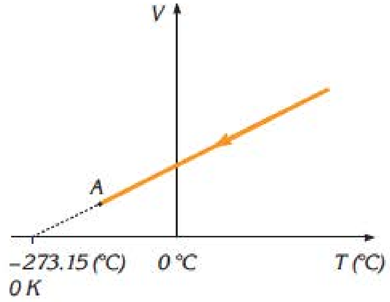


Figure 3.18 V - T graph for an isobaric process

In a real experiment, after the point A, shown in the graph, the experiment cannot continue. A real experiment involves a real gas, and a real gas turns into a liquid below a certain temperature*.

Assuming an ideal gas would continue to shrink in the same manner, without turning into a liquid, the temperature at which the volume would be zero, can be found. If a ruler is placed on the graph and the dotted line extrapolated on the graph, the temperature value corresponding to zero volume is found to be –273.15 °C. This value is taken as the 'zero' on the Kelvin scale.

Repeating the same experiment with any gas, starting from different initial conditions, always provides the same value of temperature for zero volume, as indicated in Figure 3.19.

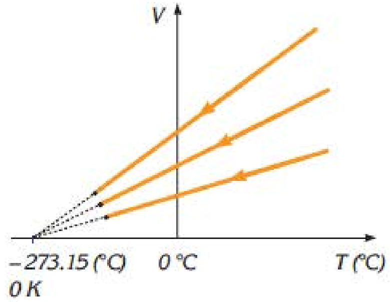


Figure 3.19 Isobars for various gases

In conclusion, the volume of an ideal gas is zero at T=0 K. Hence, the Kelvin scale is called the 'absolute temperature' scale. The 'zero' of the Kelvin scale is a real zero, there is no minus Kelvin temperature.

0 K is the lowest temperature in the universe.

Plotting a constant pressure V-T (volume versus temperature) graph on the Kelvin scale indicates a proportional relationship, as shown in Figure 3.20.

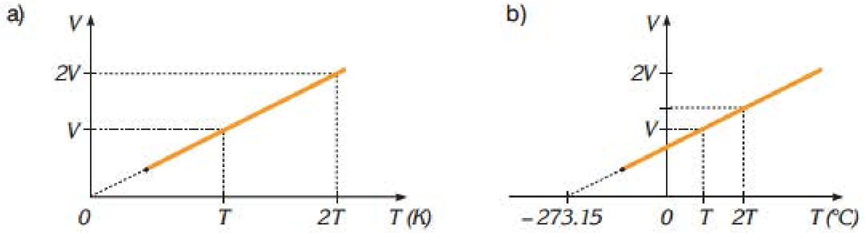


Figure 3.20 a) Volume and temperature increase proportionally on the Kelvin scale, at constant pressure. The volume of a theoretical non-liquefiable gas would be zero at 0 K. b) On the Celsius scale, volume does not increase in proportion to temperature, at constant pressure.

---

* A real gas would not produce a perfect straight line. A real gas behaves less ideally as its density increases.

On the Kelvin scale, the ratio V/T stays constant.

At constant pressure:

$$\frac{V}{T} = \text{const}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{T in Kelvins})$$

A straight line, starting from zero on the V - T (volume versus temperature) graph, indicates constant pressure. Constant pressure lines on graphs are called **isobars**. Some isobars are shown in Figure 3.21.

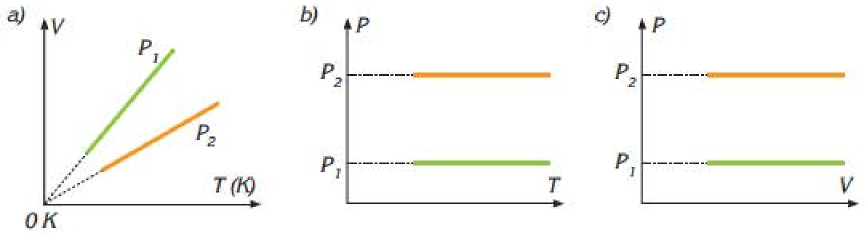


Figure 3.21 Isobars plotted on different graphs a) V-T graphs of two isobaric processes taking place at two different constant pressures b) Corresponding P-T graphs c) Corresponding P - V graphs

Question

Why is an ideal gas expected to have zero volume at 0 K?

Answer

The temperature of a gas is a measure of the average kinetic energy of its molecules.

Temperature on the absolute scale is directly proportional to the average kinetic energy. Hence, zero absolute temperature corresponds to molecules at rest. Since an ideal gas occupies volume solely because of the motion of its molecules, the volume drops to zero at 0 K.

Figure 3.22 Iso-volumetric heating

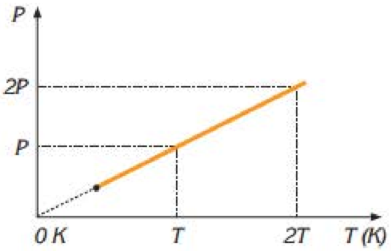


Figure 3.23 An ideal gas has zero pressure at absolute zero

Charles's Law

Pressure - temperature (P-T) relationship of a gas sample at constant, volume.

Changing the pressure and temperature of a gas sample at constant volume is called an isovolumetric process.

'**Iso-volumetric**' means occurring at 'constant volume'.

When an ideal gas is heated in a closed container, the pressure of the gas increases with increasing temperature, as shown in Figure 3.22.

Plotting a P-V volume graph on the Kelvin scale gives a graph similar to that shown in Figure 3.23.

On the Kelvin scale the P - T ratio stays constant as volume is varied.

$$\frac{P}{T} = \text{const}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (\text{T in Kelvins})$$

A straight line starting from zero on the P - T graph indicates an iso-volumetric process. Iso-volumetric lines are shown in Figure 3.24.

A real gas would liquefy at very low temperatures. The graphs below have been extrapolated after the point at which the real gas liquifies, assuming that the pressure of an ideal gas would continue to decrease in the same manner.

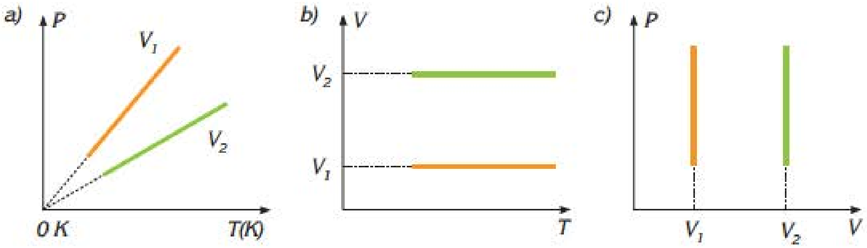


Figure 3.24 Iso-volumetric processes plotted on different graphs a) V-T diagrams graphs of two isobaric processes taking place at two different constant pressures b) Corresponding P-T graphs c) Corresponding P-V graphs

From a molecular point of view, the pressure of a gas is caused by the motion of its molecules. Since molecular motion stops at absolute (0 K), it is natural to expect pressure to be zero at this temperature. Higher temperatures mean faster moving particles. As average speed increases, molecules strike the walls of the container more forcefully, thus increasing the pressure.

Two points must be treated with caution when using the three gas relationships described above:

- In all three equations the Kelvin temperature scale must be used.
- Any unit for P and V can be used, as long as it is used on both sides.
- P in the formulas is the absolute pressure of the gas - not the gauge pressure.

Example 3.4 A rising air bubble

The volume of an air bubble becomes four times greater as it rises from the bottom to the top of a lake. What is the depth of the lake if its temperature is constant? Atmospheric pressure is measured to be 100 kPa and the density of water is 1000 kg/m^3.

Solution

The air bubble is a sample of gas surrounded by water. Assuming constant temperature, Boyle's law can be used for the air bubble.

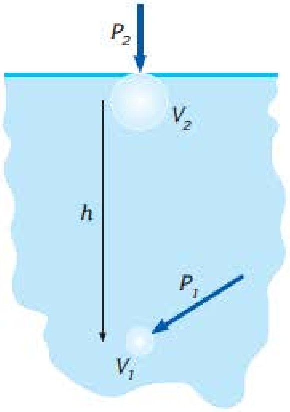


Figure 3.25 The volume of an air bubble increases as it rises upwards.

The initial pressure of the gas inside the bubble equals the liquid pressure plus the atmospheric pressure, as shown in Figure 3.25.

$$P_1 = P_0 + \rho gh$$

The final pressure just before the bubble pops equals the atmospheric pressure.

$$P_2 = P_0$$

Initial and final volumes are related as,

$$V_1 = V,\ V_2 = 4V$$

Therefore

$$P_1V_1 = P_2V_2$$

$$P_1V = P_2\,4V$$

$$P_1 = 4P_2$$

$$P_0 + \rho gh = 4\,P_0$$

$$\rho gh = 3\,P_0$$

$$h = \frac{3P_0}{\rho g}$$

$$h = \frac{(3\times10^5\,\text{N/m}^2)}{(10\,\text{N/kg})(1000\,\text{kg/m}^3)}$$

$$h = 30\text{ m}$$

Example 3.5 Heating a gas under constant pressure

The volume of a gas increases by 20 % when its temperature is increased by 55 °C, at constant pressure. What is the initial temperature of the gas?

Solution

An increase in temperature by $\Delta T = 55$ °C on the Celsius scale corresponds to $\Delta T = 55$ K increase on the absolute temperature scale.

Since pressure is constant

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V}{T} = \frac{1.2\,V}{T + 55\,K}$$

Cross multiplication gives

$$T + 55\text{ K} = 1.2\,T$$

$$0.2\,T = 55\text{ K}$$

$$T = 275\text{ K}$$

Example 3.6 Tyre pressure

A car tyre is inflated until the gauge pressure (reading of the manometer) becomes 2 atm on a day when the temperature is 0°C. What will the reading on the manometer be for the same tyre, on a hot day, when T=30°C? Assume that the volume of the tyre changes negligibly and that atmospheric pressure is $P_0 = 1$ atm.

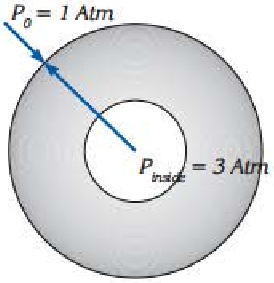


Figure 3.26 The gauge pressure is 2 atm

Solution

The first chapter shows that the manometer reads the difference between the absolute pressure of the air inside the tyre and atmospheric pressure.

This difference is called gauge pressure, as shown in Figure 3.26.

Therefore the absolute pressure of air inside the tyre at 0°C is,

$$P_{absolute} = P_{gauge} + P_0$$

$$P_{absolute} = 2\text{ atm} + 1\text{ atm} = 3\text{ atm}$$

Since volume is constant

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{3\text{ atm}}{273\text{ K}} = \frac{P_2}{303\text{ K}}$$

$$P_2 = 3.33\text{ atm}$$

Careful, this is the absolute pressure of the air in the tyre at 30°C. To find the new reading of the manometer (gauge pressure),

$$P_{gauge} = P_{absolute} - P_0$$

$$P_{gauge} = 3.33\text{ atm} - 1\text{ atm}$$

$$P_{gauge} = 2.33\text{ atm.}$$

3.5 THE IDEAL GAS LAW

The ideal gas law is the equation of state for an ideal gas, establishing the relationship between the four parameters of a gas sample. These four parameters are pressure, volume, temperature and number of moles of the gas sample. All gases behave more or less ideally at low pressures, so, when three of these four parameters are given for any gas sample, the unknown fourth parameter can be found.

Ideal gas law is an empirical physics law. It is derived from experiment and observation, rather than theory. Experiment shows that the ratio of the products

$$\frac{(\text{Pressure})\times(\text{Volume})}{(\text{Number of moles})\times(\text{Absolute temperature})}$$

equals the same constant for any gas sample.

$$\frac{PV}{nT} = \text{const.}$$

The constant in the equation is expressed as R

$$\frac{PV}{nT} = R = 8.31\ J/K$$

In the more famous form is,

$$PV = nRT$$

The constant, R, can have two different units, as shown in Table 3.2.

P	V	T	R
Pa	m^3	K	8.31 J/K
atm	lt	K	0,082 atm. lt/K

Table 3.2 The units of R, the gas constant.

Terms of mass and molar mass of the gas sample the equation becomes

$$PV = \frac{m}{M}RT$$

Example 3.7

The mass of air

Calculate the mass of air in a room with dimensions V = 5m × 4m × 3m at T = 27 °C, 1 atm pressure. Take average molar mass of air as $M_{air} = 29$ g/mole.

Solution

To determine mass, first find the number of moles.

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{(10^5 Pa)(60\ m^3)}{(8.31\ J/K)(300K)}$$

$$n \approx 2400 \text{ moles}$$

Since one mole is M = 29 g = 0.029 kg,

$$m = n \cdot M$$

$$m = 2400 \text{ moles} \times 0.029\ \frac{kg}{mole}$$

$$m = 69.6\ kg$$

Actually air is a mixture of mainly two gases, 80% nitrogen and 20% oxygen. Their molar masses are $M_{N_2} = 28$ g/mole and $M_{O_2} = 32$ g/mole

Example 3.8

The pressure of a gas mixture

A mass of 12 g of helium and 20 g of neon are enclosed in a container of volume 30 lt at 400 K. Find the absolute pressure inside the container. (Take $M_{He} = 4$ gr/mole, $M_{Ne} = 20$ gr/mole)

Solution

Inside the container is a mixture of two gases. Is the ideal gas law still applicable?

The answer is yes. Ideal gas law is applicable to any gas or mixture of gases.

To use it, we require only the number of moles of a gas. The type of gas is unimportant, as long as it behaves ideally.

Therefore, to find the total pressure, substitute the total number of moles in the container.

$$n_{total} = \frac{m_{He}}{M_{Ne}} + \frac{m_{He}}{M_{Ne}}$$

$$n_{total} = \frac{12g}{4g} + \frac{20g}{20g} = 4\,\text{moles}$$

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{(4)(8.31 J/K)(400K)}{(30\times10^{-3} m^3)}$$

$$P = 443\,200 \text{ Pa} \approx 4.4 \text{ atm}$$

Example 3.9 The density of an ideal gas

What is the density of oxygen gas at 27 °C under 1 atm pressure?

(Take M_{O_2}=32 g/mole)

Solution

Density is mass per unit volume. In the question, neither mass nor volume of the gas is given. However, the density of a gas can be found if we know the temperature and pressure.

Using the ideal gas law,

$$PV = nRT$$

$$PV = \frac{m}{M}RT$$

$$\frac{m}{V} = \frac{PM}{RT}$$

$$\boxed{\rho = \frac{PM}{RT}}$$

Therefore the density of an ideal gas is directly proportional to the pressure, and inversely proportional to the absolute temperature of the gas.

In our question,

1 atm ≈ 10^5 Pa, 27 °C ≈ 300 K

$$\rho = \frac{(10^5 Pa)\times(0.032\,kg/mole)}{(8.31 J/K)\times(300K)}$$

$$\rho = 1.29\frac{kg}{m^3}$$

Question

Can the three gas equations be derived, starting from the ideal gas law?

Answer

Yes. Some additional gas equations can also be derived.

Consider a gas sample in a container consisting of n_1 moles, having volume V_1 at temperature T_1 under pressure P_1. This can be expressed as

$$\frac{P_1V_1}{n_{1s}T_1} = R$$

If all the parameters are changed: Take some gas out of the container, decrease the pressure, and change the temperature, the final values of the parameters are then n_2, P_2, T_2, V_2.

A similar equation can be written

$$\frac{P_2V_2}{n_2T_2} = R$$

since the ideal gas law is applicable to any gas sample.

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

for any two gas samples.

To derive the gas equations, cancel the parameters that remain constant during the process.

If the amount of gas is fixed, n is constant. Writing $n_1 = n_2 = n$, the equation becomes

$$\frac{P_1V_1}{nT_1} = \frac{P_2V_2}{nT_2}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This equation is called the combined law.

3.6 EXPRESSING THE IDEAL GAS LAW IN TERMS OF NUMBER OF MOLECULES

The ideal gas law, used in the previous form, is convenient when the mass, or number of moles of a gas sample is known.

To establish a relationship between the number of molecules of a gas and its pressure, use

$$PV = nRT$$

$$PV = \frac{N}{N_A}RT$$

$$PV = N\left(\frac{R}{N_A}\right)T$$

N is the number of molecules of the gas, N_A is Avogadro's number.

Since both R and N_A are constants, their ratio must be a new physical constant. It is called the 'Boltzmann' constant' and is represented as k.

$$k \equiv \frac{R}{N_A} = \frac{8.31\ \text{J/K}}{6.02\times10^{23}} = 1.38\times10^{-23}\,\frac{\text{J}}{\text{K}}$$

Thus, the ideal gas law becomes

$$\boxed{PV = NkT}$$

Molecular Concentration

Molecular concentration is the number of molecules in unit volume. It will be represented by n_u.

$$n_u \equiv \frac{N}{V} \qquad \text{unit}:\left[\frac{\text{molecules}}{\text{m}^3}\right] = \left[\frac{1}{\text{m}^3}\right] = \left[\text{m}^{-3}\right]$$

Now the ideal gas law can be expressed in terms of molecular concentration.

$$PV = NkT \quad \Rightarrow \quad P = \frac{N}{V}kT$$

$$PV = n_u kT$$

Written in this form, the ideal gas law indicates that the pressure of a gas depends on two factors:

- Absolute temperature
- Molecular concentration

This can be explained using the molecular model of the gas. Remember, the pressure of a gas is caused by the molecules striking the walls of the container. Temperature determines how fast the molecules are striking the container, molecular concentration determines how many molecules there are.

Example 3.10

Calculating molecular concentration

What is the molecular concentration of air in your class?

Solution

Assumming T = 20 °C and P = 1 atm,

$$n_u = \frac{P}{kT}$$

$$n_u = \frac{(10^5\ \text{Pa})}{(1.38\times10^{-23}\,\text{J/K})(293\,\text{K})}$$

$$n_u \approx 2.5\times10^{25}\,\frac{\text{molecules}}{\text{m}^3}$$

Since $1\,\text{m}^3 = 10^6\,\text{cm}^3$, this value corresponds to,

$$n_u \approx 2.5\times10^{19}\,\frac{\text{molecules}}{\text{cm}^3}$$

25 million million million air molecules are flying around in each cm^3 of air around us.

The average speed of a molecule is about 500 m/s = 1800 km/h at this temperature.

One molecule undergoes about 1 000 000 000 collisions with other molecules in a second.

The air around us is not as peaceful as it looks!

3.7 THE CONSTANT VOLUME GAS THERMOMETER AND THE DEFINITION OF TEMPERATURE

The constant volume gas thermometer works on the principle that the pressure of an ideal gas sample is proportional to its absolute temperature, at constant volume. Figure 3.28 depicts a constant volume gas temperature. The volume of the gas in the balloon is kept constant by adjusting the position of the movable mercury-filled tube. The difference in height of the mercury column indicates the pressure of the gas.

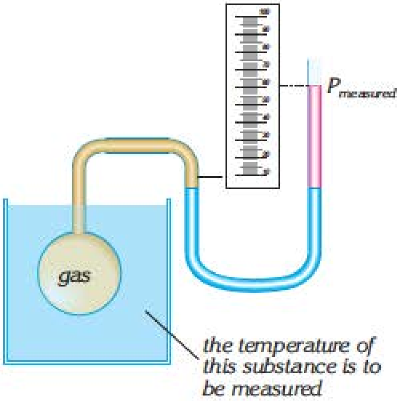


Figure 3.27 The constant volume gas thermometer

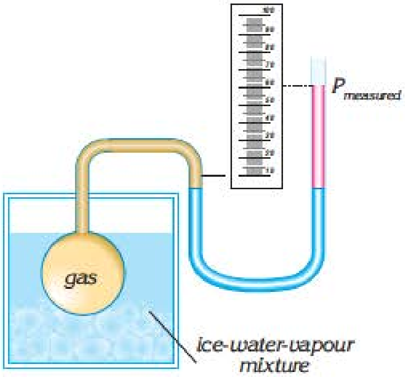


Figure 3.28 The reference pressure

At constant volume, pressure is proportional to temperature. Using a constant volume gas thermometer, we can compare the temperature of any substance with a reference temperature.

Since it is extremely stable, the reference temperature is taken as the triple point of water. Under very low pressure (4.58 mm-Hg), water, ice and vapour can exist together at a definite temperature. This unique temperature is called the **triple point of water.**

The triple point of water is defined as 273.16 K or 0.01 °C.

Therefore measuring the temperature of any substance means comparing this temperature to the triple point of water.

Suppose the temperature of a substance must be measured. The gas balloon of the constant volume gas thermometer is placed in contact with the substance, as shown in Figure 3.27. Suppose the pressure reading is P_{measured}, then the same balloon is placed in a water-ice-vapour mixture (at the triple point). Let us call the pressure of the gas in the balloon $P_{\text{reference}}$. This process is shown in Figure 3.28. Since the volume of the gas stays constant,

$$T_{\text{measured}} = \frac{P_{\text{measured}}}{P_{\text{reference}}} \times T_{\text{reference}}$$

$$T_{\text{measured}} = \frac{P_{\text{measured}}}{P_{\text{reference}}} \times 273.16\,\text{K}$$

Summary

Definitions

Temperature is a measure of the average kinetic energy of molecules

An **Isothermal process** is a process which takes place at constant temperature

An **Isobaric process** is a process which takes place at constant pressure.

An **Isovolumetric process** is a process which takes place at constant volume

Molecular concentration is the number of molecules in unit volume

$$n_u \equiv \frac{N}{V} \qquad \text{unit}: \frac{1}{m^3}$$

Laws and Principles

Ideal gas law : $PV = nRT$ or $PV = NkT$

Linear expansion : $\Delta L = \alpha L_0 \Delta T$

Other Formulas

Boyle-Mariotte law : $P_1V_1 = P_2V_2$ (T = const)

Gay-Lussac law : $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ (P = const)

Charles' Law : $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ (V = const)

Fahrenheit - Celsius conversion : $\frac{T_C}{100} = \frac{T_F - 32}{180}$

Celsius - Kelvin conversion : $T_K = T_C + 273.15$

Area expansion : $\Delta A = 2\alpha A_0 \Delta T$

Volume expansion : $\Delta V = 3\alpha V_0 \Delta T$

Density of ideal gas : $\rho = \frac{PM}{RT}$

QUESTIONS AND PROBLEMS

(Take $\rho_{water}=1000$ kg/m^3, g=10 N/kg, 1 atm = 100 kPa)

3.1 of Temperature Scales

1. Convert 37 °C into Fahrenheit and Kelvin.

2. Convert –40 °C into Kelvin and Fahrenheit.

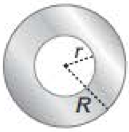
3. The temperature of oil in a pan increases from 20 °C to 300 °C while frying potatoes. Express the temperature change in Celsius and Kelvin units.

3.2 Thermal Expansion

4. Concrete and iron are used together in many buildings, since their expansion coefficients are similar. What would happen if they had different expansion coefficients?

5. The length of a railroad track is 30 m at 20 °C. Find the length of the same track at 30 °C and 0 °C. (Take $\alpha_{iron}=12\times10^{-6}$ 1/°C)

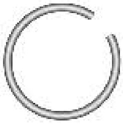
6. A hole of radius r is cut from a thin circular metal sheet, of radius R. Does the hole get larger or smaller when the metal is heated?



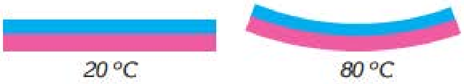
7. How can we change the density of a substance?

8. An aluminum and a steel rod are both 1 m long at 20 °C. What is the difference between their lengths at 120 °C? (Take $\alpha_{iron}=12\times10^{-6}$ 1/°C, $\alpha_{aluminum}=24\times10^{-6}$ 1/°C)

9. A circular iron ring has a small gap in its circumference, as shown in the figure. Does the width of the gap increase or decrease when the ring is heated?



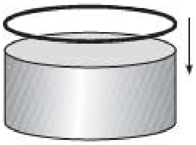
10.



A bimetallic strip (two different metal strips stuck together) takes a curved shape, as shown in the figure, with increasing temperature. Compare the expansion coefficients of the two metals. What happens when the strip is cooled below 20 °C?

11. Two rods, made of the same metal, have lengths of 1000 mm and 500 mm. Both rods are heated, so that their temperature increases by 100 °C. The length of the 1000 mm rod is then measured to be 1001 mm. What is the final length of the 500 mm rod?

12. A circular metal ring has an inner diameter of 100 mm, at 20 °C. At what temperature will it fit onto a metal cylinder, of 101 mm diameter. Only the ring is heated and the expansion coefficient for the ring's material is $\alpha=10^{-5}$ 1/°C.

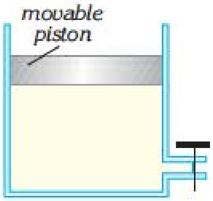


3.3 Molecular Interpretation of Temperature

13. What is the meaning of temperature, from a molecular point of view?

3.4 The Gas Laws

14. The gas in the container is in equilibrium, as shown in the figure. Which one(s) of the following actions will increase the gas pressure inside?



I. Placing mass on the piston
II. Heating the container
III. Adding gas from the tap

15. A gas is trapped in a vertical cylinder by a piston of mass 60 kg and area of 300 cm^2. The open air pressure is 100 kPa. What is the pressure of the gas inside the cylinder?

16. What is the pressure of the gas inside the cylinder in problem 15, if the cylinder is placed horizontally?

17. What does an 'isothermal' process mean? Explain how we can achieve an isothermal process.

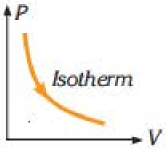
18. A gas sample occupies a volume of 60 lt, under 100 kPa pressure. What is the volume of the same gas sample under 250 kPa pressure, at the same temperature?

19. The volume of a gas sample decreases from 5 lt to 3 lt, when it is compressed isothermally. What is the final pressure of the gas, if its initial pressure is 120 kPa?

20. The pressure of a gas sample increases by 50 kPa, while it is compressed isothermally from 4 lt to 1 lt. What is the initial pressure of the gas?

21. A 24 lt container is filled with air at 100 kPa. Then it is connected with a 6 lt empty evacuated vessel. What is the final pressure of the combined system if the temperature stays constant?

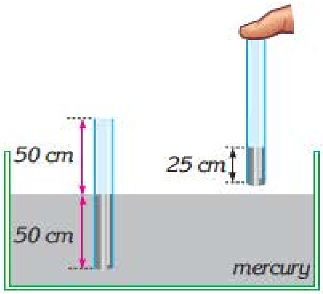
22. A P-V plot for the isothermal expansion of a gas is given in the figure. Draw the corresponding V-T graph.



23. The pressure of a gas increases from 100 kPa to 120 kPa isothermally. What is the initial volume of the gas if the decrease in volume is 4 lt?

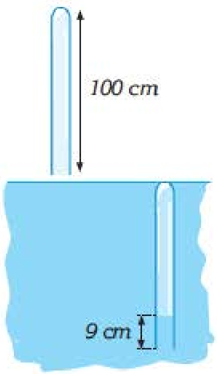
24. A 100 lt empty vessel is to be filled with air at 4 MPa (One MegaPascal=10^6 Pa). Atmospheric pressure is constant at 100 kPa. How many seconds will it take the compressor to fill the vessel, if it absorbs 200 lt of air at atmospheric pressure, in one second, at constant temperature.

25.

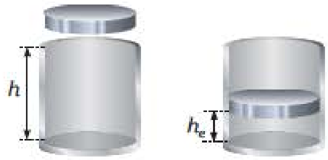


A glass tube open at both ends is dipped in mercury vertically up to half its length, as shown in the figure. The total length of the tube is 100 cm. The upper hole is then covered and the tube is vertically raised, slowly, out of the mercury bath, so that it gives rise to an isothermal process. A column of mercury of 25 cm length is observed to remain in the tube. What is the atmospheric pressure? (Hint: Use cm-Hg as the unit of pressure.)

26. A 1 m glass tube, closed at one end, is immersed in water completely. Find the open air pressure if the water rises 9 cm in the tube. Assume that the temperature remains constant.



27.

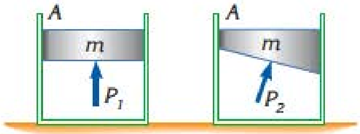


The piston in the figure is slowly lowered into the cylinder, so that it gives rise to an isothermal process. Given that the area of the piston is A=10 cm^2, the mass of the piston is 40 kg, the cylinder height is h=30 cm, and atmospheric pressure is $P_0=10^5$ Pa. What is the equilibrium height?

28. What is the reason for calling the Kelvin temperature scale the 'absolute scale'?

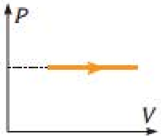
29. What is an 'isobaric process' for a gas sample? Explain how we can achieve an isobaric process.

30.

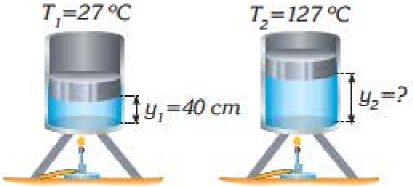


Compare the gas pressures in the identical cylinders in the figure. The masses of the pistons are equal.

31. The P-V graph of a gas sample, during a thermal process is given in the graph. Draw the corresponding V-T graph for the same process.



32.



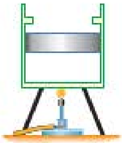
The movable piston in the figure is in equilibrium at a height of 40 cm above the bottom of the cylinder, when the temperature is 27 °C. What is the height of the piston when the temperature is 127°C?

33. The volume of an ideal gas sample triples, as its temperature increases by 300 K at constant pressure. What was the initial temperature of the gas?

34. The temperature of a gas sample is increased by 100 K isobarically. The volume of the gas increases by 20% during the process. What was the initial temperature of the gas?

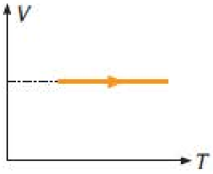
35. The temperature of a sample of gas increases from 27°C to 327°C, at constant pressure. Find the ratio of its final density to its initial density.

36. Plot the P-V graph for the cylinder-piston system shown in the figure.



37. What is an 'isovolumetric process' for a gas sample? Explain how we can achieve an isovolumetric process.

38. The V-T plot of a gas sample during a thermal process is given in the Figure. Plot the corresponding P-T graph for this process.



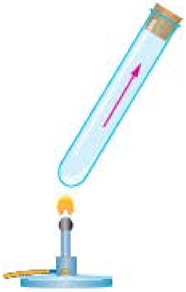
39. Absolute pressure in a sealed container is 100 kPa at 27°C. What is the pressure in the same container at 127°C?

40. The pressure of a gas increases by 20 % when its temperature is increased by 55 °C, at constant volume. What was the initial temperature of the gas?

41. An empty pressure cooker is closed at 1 atm and 27 °C. Then it is heated up to 227 °C. What is the net pressure force on the lid of area 0.1 m^2?

42. A car tyre is inflated until the gauge pressure (reading of the manometer) becomes 3 atm on a day when the temperature is 20 °C. What will the reading on the manometer be for the same tyre on a hot day, when T=40 °C? Assume that the volume of the tyre does not change and atmospheric pressure is P_0 = 1 atm.

43. A test tube containing only air is plugged with a cork, in a room where air temperature and pressure are 27 °C and 100 kPa, respectively, and the cross-sectional area of the tube is 1 cm^2. To what absolute temperature must the gas be heated to pop the cork, if the maximum friction force between the tube and the cork is 12 N?



3.5 The Ideal Gas Law

44. Avogadro's law states that 'equal volumes of all gases contain equal numbers of molecules at the same temperature and pressure'. Can we derive this principle from the ideal gas law?

45. What is the absolute pressure of 50 g neon gas kept in a 10 lt vessel at 300 K? (M_{Ne}=20 g/mole)

46. Show that one mole of any gas at STP (Standard Temperature and Pressure) occupies a volume of 22.4 lt.

47. What volume does 0.016 kg oxygen gas occupy at 57 °C, under 100 kPa pressure?(M_{O_2}=32 g/mole)

48. What is the mass of air in an 80 m^3 room at 20 °C and 1 atm of pressure? Take the molar mass of air to be M=29 g/mole.

49. A 20 lt container holds gas at 350K under 83.1 MPa (megapascals) pressure. How many moles of gas are there in the container?

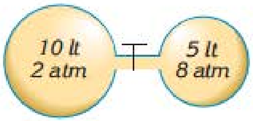
50. Helium is contained in a vessel of volume 16.62 lt, at 227 °C, under 30 atm pressure. What is the mass of helium in the vessel if the molar mass of helium is 0.004 kg/mol?

51. A gas of mass 16.8 g mass is used to fill a 24.93 lt balloon at 227 °C. What is the molar mass of the gas if the pressure is 100 kPa?

52. What is the mass of air, in an air bubble of volume 8.31 cm^3 the at a depth of 20 m below the surface of the water? The temperature at this depth is 7°C. (Take M_{air}=29 g/mole, P_0=100 kPa)

53. What is the density of nitrogen at 27 °C, under 1 atm pressure? (Take M_{N_2}=0,028 kg/mole)

54. What is final pressure of the gas, in units of atmospheres (atm), in the combined system after the valve is opened? (Temperature is constant)



55. Suppose that equal masses of two different ideal gases are mixed in a closed container. After a sufficiently long time, which of the following parameters of the gases will be equal at the end, when equilibrium is attained?

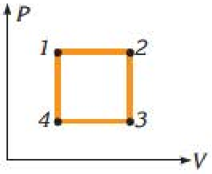
I. Total internal energy
II. Average kinetic energy of molecules
III. Volume

56. 30 g of neon and 10 g of helium are enclosed in a container of volume 20 lt. If the temperature is 300 K, what is the pressure inside the container in units of kPa? (Take M_{He}=4 g/mole, M_{Ne}=20 g/mole)

57. An open container holds 1.2 kg gas. How much gas will flow out of the container if the temperature increases from 300 K to 400 K?

58. The temperature of air in a 120-m^3 room increases from 27°C to 32 °C. What mass of air leaves the room? (Take M_{air}=0.029 kg/mole, P_0=100 kPa)

59. At which point on the P-V graph in the figure is the gas temperature a maximum?



60. An air bubble has a volume of 1 cm^3 at a depth of 10 m, under the surface of the water, in a lake whose temperature is 7°C. What is the volume of the bubble near the surface, where the temperature is 17 °C? Take atmospheric pressure to be 1 atm.

61. A gas sample is enclosed in a vessel at 400 K, under 200 kPa pressure. What will the pressure of the gas be if 40% of the gas is taken out, and the temperature is decreased to 300K?

62. One mole of air is confined in a cylinder by a movable piston having a mass of 10 kg and an area of 10^{-3} m^2. Atmospheric pressure is 100 kPa. The cylinder absorbs heat, such that its temperature increases by 20 C. What is the displacement of the piston?

3.6 Expressing the Ideal Gas Law in Terms of Number of Molecules

($k=1.38\times10^{-23}$ J/K)

63. What does 'molecular concentration' mean?

64. What is the molecular concentration of air at STP?

65. What is the pressure of an ideal gas of concentration 2.5×10^{19} molecules/cm^3 at 300 K?

66. Why does the pressure of a gas increase with increasing concentration, from a molecular point of view?

67. Estimate the total number of air molecules in your class under standard atmospheric pressure at 20 °C.

68. The pressure of a gas in a sealed balloon is 10 kPa at 200 K. What is the concentration of gas atoms in the balloon?

3.7 The Constant Volume Gas Thermometer and the Definition of Temperature

69. What does 'triple point' mean?

Heat

CHAPTER 4

Heat, internal energy and mechanical work are three important concepts in the study of thermodynamics. In this chapter the relationship between heat, temperature and internal energy will be explored. In the next chapter the role of work in the thermodynamical process will be discussed. Following this, the laws of thermodynamics will be investigated.

4.1 HEAT (Q) AND TEMPERATURE (T)

When two objects at different temperatures are in contact, the colder object warms up and the hotter object cools down; until they attain a common temperature. It seems 'something' is flowing from the hot object to the cold object.

Early scientists (up until the middle of the 19th century) explained this fact by assuming that a material substance, similar to a thin fluid, flows from hot objects to cold objects. They called this substance 'caloric'. According to this theory, hot objects contained more caloric then cold objects, and on contact caloric flowed.

Today we know that 'caloric' does not exist. Heat flow is a form of energy transfer.

Heat or heat energy is the energy transferred between two bodies as a result of a temperature difference. Heat is symbolised in physics by the letter Q.

We can explain heat transfer between two objects in terms of the motion of molecules of the objects. Consider two pieces of a metal, one hot and one cold, brought into contact, as shown in Figure 4.1. Since temperature is an indication of the speed of molecular motion, molecules of the hot piece are faster, on average, than molecules of the cold piece.

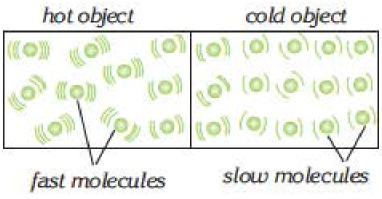


Figure 4.1 Heat flow

When brought into contact, interaction between the molecules of the two pieces, at different temperatures, eventually cause the temperatures of the substances to equalise. Fast molecules slow down as they transfer part of their individual kinetic energies to slower molecules. Hence thermal energy is transferred between molecules.

Two objects are said to be in **thermal contact** if they can exchange heat , as shown in Figure 4.2.

When two objects reach the same temperature, heat flow (energy transfer) between them ceases. Two objects, having the same temperature, are said to be in **thermal equilibrium**. This concept is shown in Figure 4.3.

Consequently, it can be said that, heat flows until the temperatures are equal.

The principle that allows us to measure temperature is called the zeroth law of thermodynamics. The **Zeroth law** states that 'If objects A and B are in thermal equilibrium with object C, then objects A and B are in thermal equilibrium with each other'.

As stated above, heat energy is the energy passing from one object to another due to the temperature difference. Therefore phrases like 'heat of an object' or 'heat contained in an object' are meaningless. One can refer to the temperature of a gas in a balloon, which provides an indication of the average kinetic energy of gas molecules; but one cannot refer to the heat of the same gas sample. The correct way of expressing heat is to refer to it as 'heat flowing into or out of the gas'.

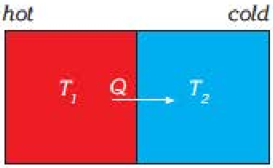


Figure 4.2 Thermal contact $T_1>T_2$

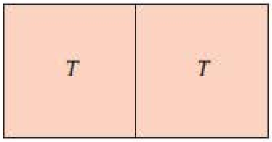


Figure 4.3 Thermal equilibrium $T_1>T>T_2$

4.2 INTERNAL ENERGY (U)

In thermodynamics, the total energy of a system is called its internal energy and is denoted by 'U'.The **internal energy** of a system is the sum of the potential and kinetic energies of the molecules in the system. The term **thermal energy** also has the same meaning*.

Note that, the motion of an object as a whole does not contribute to its internal energy. Two bottles of water at the same temperature, one at rest, the other moving at 120 km/h on a bus, have the same internal energy.

Internal Energy of Gases

The force between the molecules of an ideal gas is zero, unless two molecules collide. In other words, molecules of an ideal gas do not 'see' each other from a distance. Gas molecules are not bound to each other, and are free to move around. Therefore the potential energy, due to intermolecular forces, for gas molecules is zero.

Gas molecules can only have kinetic energy. The internal energy of a gas is the sum of all the kinetic energies of the molecules.

$$U_{gas} = (KE)_{total} \text{ of gas molecules}$$

Since temperature is a measure of the average kinetic energy of the molecules, the total internal energy of a gas sample is proportional to the temperature and number of molecules.

Internal Energy of Solids and Liquids

In Chapter 2, molecules forming a solid or liquid were discussed in terms of their intermolecular forces. Molecules are not stationary: In solids they oscillate about equilibrium positions, in liquids they both oscillate and slip over each other.

Therefore, molecules of a solid or liquid have both kinetic and potential energies of their intermolecular bonds. Thus

$$U_{\text{solid or liquid}} = (KE)_{total} + (PE)_{total} \text{ of molecules}$$

Due to the complexity of interactions between molecules, a simple expression cannot be derived for the internal energy of a solid or liquid, as is possible for gases.

---

* There is a difference between these two concepts. The thermal energy of a substance is the energy related to the thermal motion (see chapter 2) of molecules of that substance. On the other hand, internal energy of a substance is the sum of all energies possessed by the molecules of that substance. These energies may include chemical, electrical, nuclear, etc... and thermal energies. Thermal energy is a part of the internal energy, and it changes with temperature.

However, we can use the terms 'internal energy' and 'thermal energy' interchangeably. Since only the change in energy is important. During a thermodynamical process; such as heating a solid or compressing a gas, change in internal energy is the change in thermal energy. Nuclear and chemical energies do not change during a thermodynamical process.

When a gas absorbs energy from its surroundings, its temperature increases. Since gas molecules do not have intermolecular potential energy, all the energy is converted into kinetic energy of the molecules; raising the temperature.

On the other hand, energy transferred to a solid or liquid may not always change its temperature. As discussed in this chapter, the temperature of a solid stays constant as it melts. The energy given to the solid, during melting, is used to break the bonds between the solid molecules.

In short, an increase in temperature indicates an increase in internal energy for all substances, solids liquids or gases. However, the internal energy of a solid or liquid can be changed without changing its temperature.

4.3 THE MECHANICAL EQUIVALENT OF HEAT

The old unit of heat is the calorie (cal). The calorie was defined before it was understood that heat was a form of energy flow.

1 cal is the amount of heat required to raise the temperature of 1 g of water by 1 °C.

Incidentally the unit 'Calorie' with an upper case C (also defined as 'big calorie' or 'food calorie'), is used by nutritionists to characterise the energy-producing potential in food.

$$1 \text{ Cal} = 1 \text{ kcal} = 1000 \text{ cal.}$$

The equivalence of heat and mechanical energy was realised by five different people (not all of them scientists) in the middle of the 19^{th} century. The scientist Joule first calculated the mechanical energy equivalent of heat in 1845; thus, the unit of energy is the Joule (J). The accepted value for the mechanical equivalent of heat today is

$$1 \text{ cal} = 4.184 \text{ J}$$

Although today it is known that heat is a form of energy transfer, the unit 'calorie' is still in use.

Example 4.1

Burning sugar

The energy content of 1g of sugar is about 4 Cal (= 4000 cal). Suppose the energy content in 10 g sugar is completely turned into electric energy and used to light a 100-Watt light bulb. How long will the lamp operate?

Solution

10 g sugar contains 40 000 cal. The Joule equivalent of this energy is

$$40000 \text{ cal} \times 4.18 \frac{\text{J}}{\text{cal}} = 167200 \text{ J}$$

Since $1 \text{ Watt} \equiv 1 \frac{\text{J}}{\text{s}}$ the duration can be found by

$$\text{time} = \frac{\text{energy}}{\text{power}}$$

$$t = \frac{167200 \text{ J}}{100 \text{ W}} \approx 1672 \text{ sec}$$

$$t \approx 28 \text{ min}$$

Example 4.2

Keeping fit

A 70-kg man eats a large lunch which supplies him with 2500 Cal. How high an apartment must this man climb (by the stairs) to consume all the energy he absorbed from his meal?

Solution

2500 Cal = 2 500 000 cal, which corresponds to 10 450 000 J.

As the man climbs the stairs, the energy supplied by the food, turns into the potential energy he would have at the top of the apartment of height, h.

Writing the equality

Energy from food = mgh

10450000 J = mgh

$$h = \frac{10\,450\,000 \text{ J}}{(70 \text{ kg}) \times (9.8 \text{ N/kg})}$$

$$h = 15\,233 \text{ m}$$

This is nearly twice the height of Mount Everest.

The result of the example above is interesting. Considering the fact that 2500 food Calories is found in about 300 g fat, we may wonder how most of us do not get very fat, though we do not climb Mount Everest everyday.

The reason is that, the energy content of sugar and fat given above are values obtained by burning them in a calorimeter and measuring the heat given off. Our bodies do not use all the energy from food.

Also most of the energy intake from food is used for the internal workings of our body, which keeps us alive at a constant body temperature of 36.5 °C. The organic processes that are necessary for life is called the metabolism. The rate of metabolism for a 70 kg person, taking a rest (energy needed for the heart to beat, blood to circulate etc...) is about 85 W (= 85 J/s). That is, the body changes 85 J of chemical energy from food into thermal energy in one second. Heavy physical activity can increase the rate of the metabolism by a factor of 10. So the man in the example could burn his meal in 34 hours just by sleeping.

4.4 SPECIFIC HEAT AND HEAT CAPACITY

Place 200 g of water and 200 g of iron over the same gas burner. Both substances absorb nearly equal amounts of heat energy from the burner. One minute later, the piece of iron will be untouchably hot, whereas the water is still warm. Different substances require different amounts of heat, for the same temperature change. The specific heat of a substance indicates this requirement.

The Specific heat of a substance is defined as the amount of heat energy needed to raise the temperature of unit mass of that substance by 1 °C.

The symbol of specific heat is the letter 'c'.

$$c \equiv \frac{Q}{m\Delta T} \qquad \text{Units}: \frac{\text{cal}}{\text{g}\,°\text{C}}, \ \frac{\text{J}}{\text{kg}\,°\text{C}}$$

Each substance has its own specific heat. Table 4.1 lists the specific heats of different substances under 1 atm pressure*.

The specific heat of a substance slightly varies with temperature. The values in the table are measured at about room temperature.

Substance	cal/g °C	J/kg °C
Water	1.0	4184
Aluminum	0.21	879
Iron	0.11	460
Ice	0.50	2 092
Copper	0.093	389

Table 4.1 Specific heats of various substances

We can find the conversion factor between $\frac{\text{cal}}{\text{g}\cdot°\text{C}}$ and $\frac{\text{J}}{\text{kg}\cdot°\text{C}}$.

$$1\frac{\text{cal}}{\text{g}\cdot°\text{C}} = \frac{(4.184\,\text{J})}{(10^{-3}\text{kg})(°\text{C})} = 4184\frac{\text{J}}{\text{kg}\cdot°\text{C}}$$

From the definition of specific heat, we can express the heat needed to increase the temperature of m grams of a substance by ΔT

$$Q = mc\Delta T$$

The specific heat is defined for a specific *substance*. We can also define *'heat capacity'* for an *object*.

The heat capacity (C) of an object is the amount of heat energy needed to raise the temperature of that object by 1 °C. The symbol, upper case 'C' is used to express this quantity.

$$C \equiv \frac{Q}{m\Delta T} \qquad \text{Unit}: \frac{\text{cal}}{°\text{C}}, \frac{\text{J}}{°\text{C}}$$

The heat formula is, $Q = C\Delta T$ for an object.

Note that, specific heat is defined for substances; heat capacity is defined for objects. The specific heat of iron can be referred to in general, but the heat capacity of a 'hammer object' made of iron must be referred to.

Example 4.3

Heating iron

How much heat is needed to increase the temperature of 200 g of iron from –15 °C to 45 °C?

Solution

First determine the change in temperature,

$$\Delta T = T_f - T_i = 45\,°\text{C} - (-15\,°\text{C})$$

$$\Delta T = 60\,°\text{C}$$

Now find heat required,

$$Q = mc\Delta T$$

$$Q = (200\,\text{g}) \times \left(0.11\,\frac{\text{cal}}{\text{g}\cdot°\text{C}}\right) \times (60\,°\text{C})$$

$$Q = 1320\,\text{cal}$$

---

* Pressure is defined, because specific heat values of substances slightly change with pressure. Chapter 5 discusses the reason for this.

Example 4.4

Cooling iron

How much heat is released when 30 g aluminum cools from 50 °C to 10°C ?

Solution

The change in temperature is,

$\Delta T = 10\ °C - 50\ °C$

$\Delta T = -40\ °C$

The negative value of ΔT indicates a decrease in temperature. To find the heat energy

$Q = mc\Delta T$

$$Q = (0.03\text{kg})\left(879\frac{\text{J}}{\text{kg}\cdot °\text{C}}\right)(-40°\text{C})$$

$Q \approx -1055\ \text{J}$

Negative heat indicates that heat is released from the system.

4.5 MECHANICAL ENERGY - THERMAL ENERGY CONVERSION

Heat energy added to a system generally turns into internal energy. This is so common an observation that, the term 'heat' is sometimes mistakenly used in place of 'internal energy' or 'thermal energy'. When a substance is heated, either its temperature rises, (increase in kinetic energy of the molecules) or the substance melts or vapourises (increase in potential energy of the molecules).

Heat given to a substance can be used for reasons other than increasing the internal energy. This will be discussed in the next chapter.

Additionally, heating is not the only way of increasing the thermal energy of a substance. This can be observed by rubbing your hands together. The increase in temperature you feel is not caused by touching a hot object. It is caused by the force of friction between your hands.

Consider the block in figure 4.4, given an initial velocity on a rough, level surface.

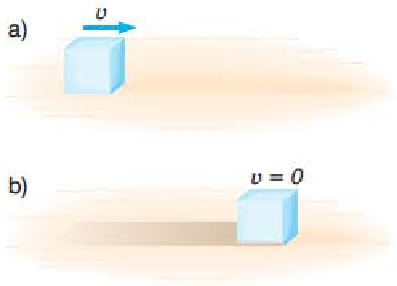


Figure 4.4 a) The object has a kinetic energy b) The object is stopped by the friction force. Kinetic energy is zero.

The kinetic energy of the object in Figure 4.4a is converted into thermal energy by the friction force. Now, both the object and the path are hotter, indicating higher thermal energy.

In general **friction turns mechanical energy into thermal (internal) energy;**

There is no simple formula for the internal energy of solids or liquids.However, there is a formula for the heat transferred to an object. In most cases heat absorbed by an object is completely converted into thermal energy. In such cases we can use the heat formula to calculate the internal energy change.

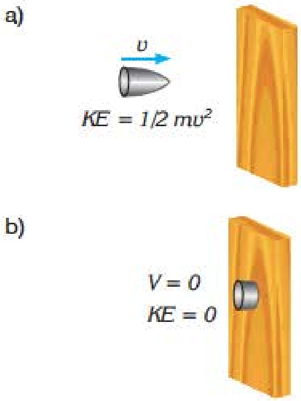


Figure 4.5 Temperature increase by impact

Example 4.5 Temperature increase by impact

A lead bullet moving at v = 200 m/s strikes and is embedded in a wooden wall, as shown in Figure 4.5. By how much does the temperature of the bullet increase? Assume that 70% of the heat produced by the impact is absorbed by the bullet. (Take $c_{lead} \approx 126$ J/kg °C)

Solution

Initially the bullet has kinetic energy, 70 % of this energy is converted into thermal energy of the bullet by the impact.

70% of KE ⇒ Increase in thermal energy of bullet

$$0.7\left(\frac{1}{2}mv^2\right) = \Delta U_{bullet}$$

The bullet does not receive any heat. The energy is produced by the impact.

The molecules of the bullet do not differentiate between the source of the energy they receive. The same amount of energy coming from a collision or from a flame causes the same temperature difference.

Thus,

$$0.7\left(\frac{1}{2}mv^2\right) = mc\Delta T$$

Note that the left side of the equation represents mechanical energy, whose unit is the Joule. Since the dimensional equivalent of the joule is $\left[\frac{\text{kg}\cdot\text{m}^2}{\text{s}^2}\right]$, calories or grams cannot be used on the right-hand side of the equation.

Simplification gives,

$$\Delta T = 0.7\left(\frac{v^2}{2c}\right)$$

$$\Delta T = 0.7 \times \frac{(200\,\text{m/s})^2}{2 \times (126\,\text{J/kg}\,°\text{C})}$$

$$\Delta T = 111\,°\text{C}$$

Why wasn't the mass of the bullet required for the solution?

4.6 CALORIMETRY

A **calorimeter** is a specially designed container which - ideally - prevents all heat transfer between its contents and the surroundings. The common thermos flask is an everyday example of a calorimeter.

As expected from the law of conservation of energy, the total thermal energy of a system inside a calorimeter remains constant. If two objects, one hot and one cold, are placed in a calorimeter, they exchange thermal energy (heat flows between them) until they attain a common temperature. Since the total energy of the system remains constant, the amount of heat released by the hot substance must be equal to the amount of heat absorbed by the cold substance.

Consider two objects A and B, exchanging 50 J heat as shown in Figure 4.6.

As we saw in examples 4.3 and 4.4 above, heat released by an object is defined to be negative; heat absorbed by an object is defined to be positive This sign convention is shown in Figure 4.7.

The magnitudes of heat released and absorbed are equal, one being positive the other negative. Thus, the sum of all heat exchanges in a calorimeter is zero

$$Q_{net} = 0$$

In other words, the magnitudes of the heats emitted and absorbed are equal

$$|Q_{given}| = |Q_{absorbed}|$$

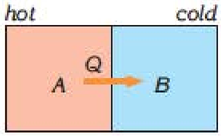


Figure 4.6 Heat exchange between two objects

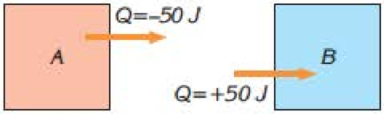


Figure 4.7 The sign convention for heat transfer.

Example 4.6 The Temperature of a mixture

200 g of water at 90.0 °C is mixed with 100 g of alcohol at 10.0 °C. Find the final temperature of the mixture. (Take $c_{alcohol} = 0.60$ cal/g °C)

Solution

The heat energy released by the water is absorbed by the alcohol.

In calorimeter problems it is generally very useful to draw a graph, indicating temperature changes of substances versus heat exchanged. Such a plot is shown in Figure 4.8

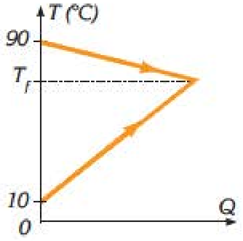


Figure 4.8 Heat released by the water is absorbed by the alcohol

$$Q_{net} = 0$$

$$\text{Heat released by water}| = |\text{Heat absorbed by alcohol}|$$

$$|m_{water}\, c_{water}\, \Delta T_{water}| = |m_{alcohol}\, c_{alcohol}\, \Delta T_{alcohol}|$$

$$\left|(200\text{ g})\left(1\frac{\text{cal}}{\text{g °C}}\right)(T_f - 90\text{ °C})\right| = \left|(100\text{ g})\left(0.6\frac{\text{cal}}{\text{g °C}}\right)(T_f - 10\text{ °C})\right|$$

$$(180\text{ °C} - 2T_f) = (0.6\, T_f - 6\text{ °C})$$

$$2.6\, T_f = 186\text{ °C}$$

$$T_f = 71{,}5\text{ °C}$$

4.7 PHASE CHANGE

Matter on Earth is normally found in three states: solid, liquid and gas. The transition between these states is called a phase change.

$$\text{solid} \underset{\text{solidification}}{\overset{\text{melting (fusion)}}{\rightleftarrows}} \text{liquid} \underset{\text{condensation}}{\overset{\text{vaporisation}}{\rightleftarrows}} \text{gas}$$

Suppose we place a block of ice initially at –30 °C in a glass beaker and place the beaker on a gas burner. Then we measure the temperature in equal time intervals. Assuming that the heat absorbed by the ice (and then water), in equal time intervals, remains the same. A heat temperature graph can be plotted as the substance changes phase from ice to vapour, as shown in Figure 4.9.

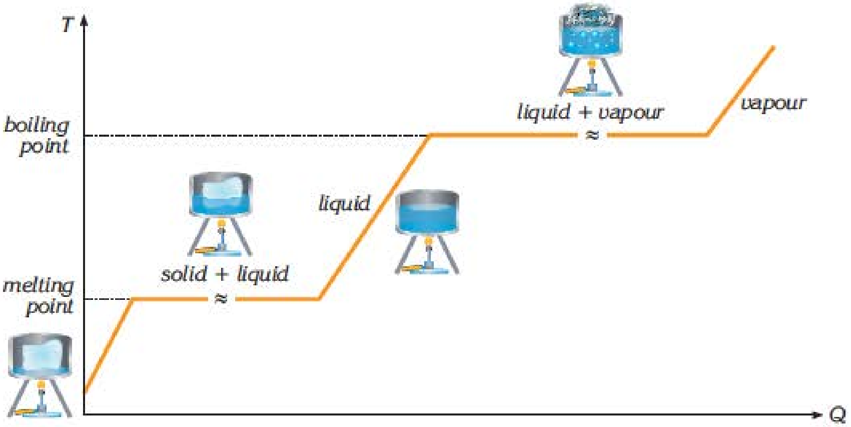


Figure 4.9 The heat - temperature graph of the phase transition from ice to vapour

The diagram above shows that, during melting and boiling, the temperature stays constant, although the substance continues to absorb heat energy. Heat absorbed during a phase change is called the **latent heat**.

Latent heat is used to break the bonds between the molecules in the solid or liquid structure. In other words, heat absorbed during a phase change is used to increase the distance between molecules, changing the potential energy only. Since the average kinetic energy of molecules does not change, the temperature remains constant.

The magnitude of latent heat depends upon the temperature or pressure at which the phase change occurs. The values listed in Table 4.3 are measured under 1 atm of pressure, at the melting and boiling points indicated in Table 4.2.

Material	Melting point (°C)	Boiling point (°C)
Oxygen	–219	–183
Water	0	100
Aluminum	660	2 450
Lead	327	1 750

Table 4.2 The melting and boiling points of various substances at 1 atm.

Material	L_f (kJ/kg)	L_v (kJ/kg)
Oxygen	13.8	210
Water	335	2 260
Aluminum	397	10 500
Lead	23	858

Table 4.3 Latent heats of fusion and vapourisation of various substances at 1 atm.

Latent heat is represented by the letter 'L'.

Latent heat of fusion (L_f) is the amount of heat energy needed to melt unit mass of a crystalline solid;

$$L_f = \frac{Q}{m} \qquad \text{unit : } \frac{\text{cal}}{\text{g}} \text{ or } \frac{\text{J}}{\text{kg}}$$

The same amount of heat is released when unit mass of the same substance solidifies. The heat formulas are thus

$$Q = mL_f \quad \text{for melting, and}$$

$$Q = -mL_f \quad \text{for solidification.}$$

This fact explains why the weather is generally warm while it is snowing, but relatively cold on a sunny day while the snow on the ground is melting. Water releases energy, to change phase into snow crystals; heating the air. Conversely, during melting, the snow absorbs heat energy from the surroundings.

The **melting point** of a substance is affected by external pressure and purity. Most substances expand during melting. Increasing the external pressure on such a substance causes a rise in the melting point of the substance.

On the other hand, a few substances, like water, contract as they melt. Increasing the pressure has an adverse effect on the melting point of such substances. It is possible to join two pieces of ice by just pressing them together. Increased pressure melts the ice by decreasing the melting point. When the pressure is removed, the liquefied ice re-freezes, sticking the pieces together.

Purity also affects melting point. In general, impurity depresses the melting point. For example, salt water freezes below 0 °C.

Latent heat of vapourisation (L_v) is the amount of heat needed to vapourise unit mass of a substance;

$$L_v \equiv \frac{Q}{m} \qquad \text{unit} : \frac{\text{cal}}{\text{g}} \text{ or } \frac{\text{J}}{\text{kg}}$$

The same amount of heat is released when unit mass of the same substance condenses. The heat formulas are

$$Q = mL_v \quad \text{for vapourisation}$$

$$Q = -mL_v \quad \text{for condensation.}$$

The physical process of boiling also involves a phase change from the liquid state state to the vapour state. However, boiling and vapourisation are different processes. In chapter 7 boiling and vapourisation will be discussed in detail. It will be seen that vapourisation occurs at all temperatures. Boiling occurs at a specific temperature, which is called the boiling point of a substance. The boiling point depends on the external pressure applied on the liquid.

During boiling, the temperature of a liquid remains constant. The heat energy absorbed from the surroundings is used for vapourisation. Increasing the heat energy available, increases the vapourisation rate, however, the temperature remains constant until all the liquid has boiled away.

As an example, we cannot make a meal (say soup) cook faster by increasing the cooker's flame, after the liquid has started to boil. Supplying more heat does not increase the temperature of the soup, as long as there is juice to vapourise. It just increases the vapourisation rate.

The graphs in Figure 4.10. summarise the heat - temperature - phase change relationship.

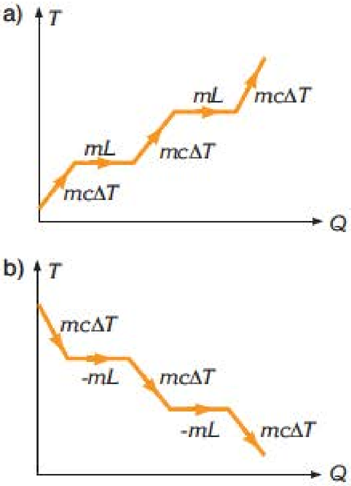


Figure 4.10 Reverse processes

Example 4.7

Melting lead

How much heat is needed to melt 200 g of lead at 327 °C?

Solution

327 °C is the melting point of lead. So the heat absorbed by to the substance will only cause a phase change at constant temperature, as shown in Figure 4.11.

Figure 4.12 shows a heat - temperature graph for the process.

$Q = mL_f$

$Q = (0.2 \text{ kg}) (23 \text{ kJ/kg})$

$Q = 46 \text{ kJ}$

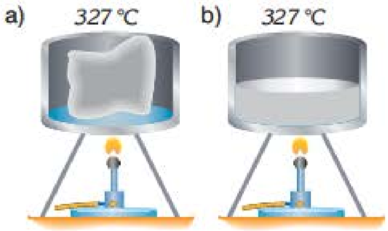


Figure 4.11 Temperature remains constant until all the solid has melted

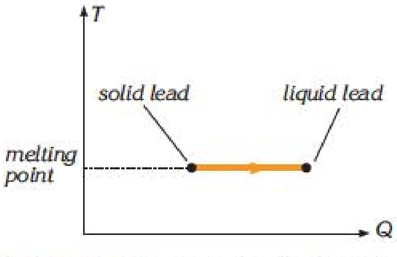


Figure 4.12 A temperature-heat graph for melting lead.

Example 4.8

Vapourising water

A 2000-W electric kettle contains 1-kg of water at 20 °C. How many minutes after the power is switched on, is 400 g water left in the kettle?

Solution

The temperature of water must reach 100 °C before it starts to boil. First, all the 1 kg mass of water is heated up to 100 °C, then 600 g boils away.

$$Q = m_{water}c\Delta T + m_{vapourised}L_v$$

$$Q = (1\ \text{kg})\ (4\,200\ \text{J/kg °C})\ (80\ \text{°C}) + (0.6\ \text{kg})\ (2\,260\ \text{kJ/kg})$$

$$Q = 336\,000\ \text{J} + 1\,356\,000\ \text{J}$$

$$Q = 1\,692\,000\ \text{J}$$

To find time required

$$\text{time} = \frac{\text{Energy}}{\text{Power}}$$

$$t = \frac{1\,692\,000\ \text{J}}{2\,000\ \text{W}}$$

$$t \approx 846\ \text{s} \approx 14\ \text{min}$$

4.8 HEAT OF COMBUSTION (q)

The heat of combustion of a fuel is the amount of heat energy given off when unit mass of the fuel burns. If the burning fuel has a mass m, the total heat obtained from combustion is

$$Q = mq$$

For example, the heat of combustion for gasoline is $q = 50 \times 10^6 \frac{\text{J}}{\text{kg}} = 50 \frac{\text{MJ}}{\text{kg}}$, the heat of combustion for diesel fuel is $q = 42 \times 10^6 \frac{\text{J}}{\text{kg}} = 42 \frac{\text{MJ}}{\text{kg}}$. In other words 1 kg diesel fuel gives off 42 000 000 J heat energy when it burns.

4.9 HEAT TRANSFER

Heat energy is transferred in three ways: Conduction, convection and radiation.

Conduction is the transfer of heat through a substance by means of the interactions between molecules. Imagine an iron rod of 1 m length being heated on one side, as shown in Figure 4.13. Imagine fast molecules on the hot side interact with the slow molecules on the colder side, making them oscillate faster.

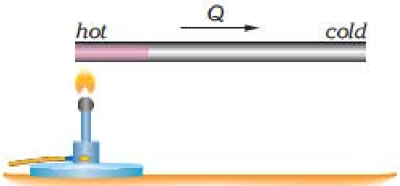


Figure 4.13 Conduction means heat flow through a material

Various factors affect the amount of heat energy flowing in one second. Consider a wall of thickness d. On each side of the wall, (inside and outside the house) the temperatures are different. Suppose on a winter's day the outside temperature, T_2 is constant and the inside temperature, T_1 is kept constant by a heater.

Heat energy flowing in unit time through the wall from inside the house to the outside is directly proportional to three factors, as shown in Figure 4.14:

Cross-sectional area of the wall (A), difference between the temperatures on both sides (ΔT) and the thermal conductivity (k) of the material from which the wall is built.

The heat flow in unit time is inversely proportional to the thickness of the wall (d).

The formula used to express this is:

$$\frac{\Delta Q}{\Delta t} = kA\frac{T_1 - T_2}{d} \qquad T_1 > T_2$$

Where k is a characteristic property of the material called the **thermal conductivity**.

$\frac{\Delta Q}{\Delta t}$ is the rate of heat flow (heat transferred in one second). Its unit is $\left[\frac{\text{energy}}{\text{time}}\right]$. In SI units this is $\frac{\text{Joule}}{\text{Second}} = \text{Watt}$. Hence the unit for thermal conductivity (k) is $\frac{W}{m \cdot {}^\circ C}$.

Materials with a large thermal conductivity are called conductors, materials with a low conductivity are called insulators. Conductivity values for substances material are listed in Table 4.3.

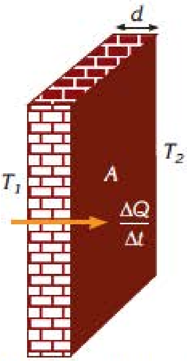


Figure 4.14 Factors affecting the rate of heat transfer

Convection is the transfer of heat through a fluid (liquid or gas) by the transfer of heated matter. Contrary to conduction, molecules of the liquid or gas undergo a net displacement during convection, as shown in Figure 4.15.

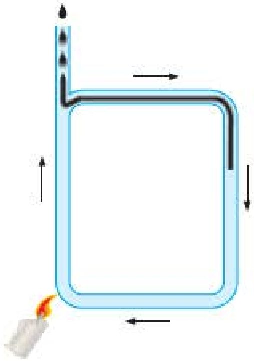


Figure 4.15 The Convection process can be observed by dropping ink into water, circulating due to convection (when it is heated at one part of its circuit).

Imagine placing your finger at a distance of 2 mm from a candle flame. How long can you hold your finger there? The answer depends on the location of your finger.

Points A and B in Figure 4.16 are the same distance away from the flame, but the temperature of point A is about 1300 °C, whereas, the temperature of point B is not much greater than room temperature.

The difference arises from the method of heat transfer from the flame to the two points.

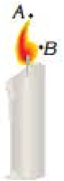


Figure 4.16 Comparing conduction, convection, and radiation using a candle flame.

Point A is heated mainly by convection, because the heated air moves upwards, not sideways. On the other hand, point B is heated by conduction and radiation, and air is a poor conductor. The warmth we feel is due to radiation from the flame.

The poor conductivity of air is the reason such good insulation is provided for animals by their fur. The air trapped between the hairs serve as an insulating layer, as shown in Figure 4.17. For the same reason, wool clothing keeps people warmer than synthetic fabrics. This also explains why even a gentle wind feels so cold in cold weather. Wind removes the layer of still air surrounding us.

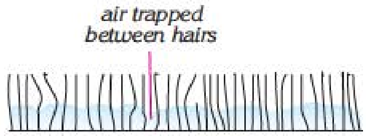


Figure 4.17 Stationary air in fur or hair provides insulation

Material	Conductivity (W/m°C)
Copper	400
Aluminum	240
Glass	0.8
Brick	0.6
Wood	0.08
Fat	0.02

Table 4.4 A table of thermal conductivities for various substances

Radiation is the transfer of heat by electromagnetic waves, especially infrared rays. Contrary to conduction or convection, radiation does not require a material medium between the hot and cold object. Energy from the Sun, for example, reaches the Earth by radiation, since there is no material medium in between.

The amount of heat energy radiated in one second from an object is proportional to the:

a) Fourth power of its absolute temperature (T^4)

b) Surface area of the object (A)

c) Emissivity factor of the material (e)

Emissivity is a number between 0 and 1. For black surfaces emissivity is close to 1, for shiny surfaces emissivity is close to 0.

A surface emits and absorbs heat energy by radiation. Black surfaces emit and absorb radiation more than shiny surfaces. In other words good emitters are good absorbers.

Summary

Definitions

Heat is the energy transferred between two bodies as a result of a temperature difference.

Two objects are in **thermal contact** if they can exchange heat.

Two objects having the same temperature are in **thermal equilibrium**.

The **internal energy** or **thermal energy** of a system is the sum of the potential and kinetic energies of the molecules in the system.

1 **calorie** is the amount of heat required to raise the temperature of 1 g of water by 1 °C.

Specific heat (c) of a substance is defined as the amount of heat energy needed to raise the temperature of unit mass of that substance by 1 °C.

$$c \equiv \frac{Q}{m\Delta t} \qquad \text{unit}: \frac{J}{kg{\cdot}°C}$$

The **heat capacity** of an object is the amount of heat energy needed to raise the temperature of that object by 1 °C.

$$C \equiv \frac{Q}{\Delta T} \qquad \text{unit}: \frac{J}{°C}$$

The **latent heat of fusion** (L_f) is the amount of heat energy needed to melt unit mass of a crystalline solid.

$$L_f \equiv \frac{Q}{m} \qquad \text{unit}: \frac{J}{kg}$$

The latent heat of vapourisation (L_v) is the amount of heat needed to vapourise unit mass of a substance

$$L_v \equiv \frac{Q}{m} \qquad \text{unit} : \frac{J}{kg}$$

The heat of combustion (q) of a fuel is the amount of heat energy released when unit mass of the fuel burns

Laws and Principles

Heat flows between two points until their temperatures are equal.

The Zeroth law of thermodynamics: If objects A and B are in thermal equilibrium with an object C, then objects A, B and C are in thermal equilibrium with each other.

Friction converts mechanical energy into thermal energy.

Heat energy is transferred in three ways: Conduction, convection and radiation

Rate of heat flow by conduction;

$$\frac{\Delta Q}{\Delta t} = kA\frac{T_1 - T_2}{d}$$

Other Formulas

Heat needed to increase the temperature of m grams of a substance by ΔT

$$Q = mc\Delta T$$

Heat needed for a substance of mass m to change phase

$$Q = mL$$

QUESTIONS AND PROBLEMS

(Take 1 cal=4.2 J, c_{water}=1 cal /g °C = 4 200 J/kg °C, g=10 N/kg)

4.1 Heat (Q) and Temperature (T)

1. Define heat.

2. Explain the terms 'thermal contact' and 'thermal equilibrium'.

3. Write down the zeroth law of thermodynamics.

4. What is wrong with the phrase 'heat of a substance'?

4.2 Internal Energy (U)

5. Define internal energy.

6. What is the difference between the internal energy of a gas and the internal energy of a liquid?

7. Can we change the internal energy of an ideal gas sample without changing its temperature?

8. Can we change the internal energy of a solid object without changing its temperature? Give an example.

4.3 The Mechanical Equivalent of Heat

9. How was the old heat unit 'calorie' defined?

10. The energy content of 1g fat is about 9 kcal. Suppose the energy content in 10 g fat is completely turned into electric energy and used to light a 100-Watt light bulb. How long will the lamp burn?

11. A man eats a dinner which supplies him with 1500 kcal energy in chemical form. How many hours will it take for him to use this much energy, if the average rate of energy consumption in his body is 100 W?

4.4 Specific Heat and Heat Capacity

12. Define specific heat for a substance.

13. Differentiate between specific heat and heat capacity.

14. Express $1\frac{\text{cal}}{\text{g}\cdot{}^{\circ}\text{C}}$ in $\frac{\text{kJ}}{\text{kg}^{\circ}\text{C}}$.

15. How much heat is needed to increase the temperature of 200 g of aluminum from –30 °C to 50 °C? (c_{Al}=900 J/kg °C)

16. The temperature of 300 g of a metal increases by 80 K upon receiving 3 120 J of heat. What is the specific heat of this metal in units of $\frac{\text{J}}{\text{kg}\ {}^{\circ}\text{C}}$?

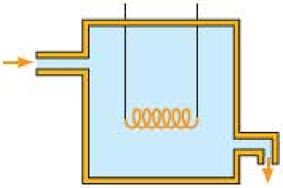
17. What is the heat capacity of a 5 g coin made of pure copper? (c_{copper}=0.09 cal/g°C)

18. How much energy is given out when 500 g iron cools from 350 °C to –150 °C? (c_{iron} = 450 J/kg °C)

19. We must heat 10 lt of water from 20°C to 80 °C, using an electric heater. We have two electric heaters; one has a power rating of 1000 W, the other 2000 W. Which heater should be used if we want to pay less for the electricity? Assume no heat loss to the surroundings.

20. How long will it take to increase the temperature of 15 lt of water from 20 °C to 80 °C using a 2000 W electric heater?

21. An instant electric heater heats water, flowing at a rate of 1.2 kg/min, from 10°C, to 100 °C. Find the power of the heater.



4.5 Mechanical Energy - Thermal Energy Conversion

22. A ball strikes a wall with 30 J of kinetic energy and bounces back from the wall with 18 J of kinetic energy. What is the amount of thermal energy produced during the collision?

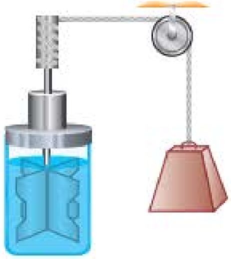
23. An object of weight 10 kg is dropped into water from a height of 21 m. What is the mass of water, if the temperature of water increases by 0.01°C? Neglect air friction and assume all the thermal energy produced is absorbed by water.

24. Assume that 50 % of the potential energy of a raindrop turns into internal energy of the drop, as it falls with constant speed due to air friction. From what height must the drop fall for its temperature to increase by 1°C?

25. A small iron ball,dropped from a height of 1 m, rebounds back to a height of 30 cm, from the floor. By how many degrees does the temperature of the ball increase? Assume all thermal energy produced by the impact is absorbed by the ball. (Take c_{iron} = 450 J/kg °C)

26. A 5-kg iron block released from a height of 200 m, reaches the ground at a speed of 30 m/s. What is the temperature of the block just before it strikes the ground, if its initial temperature is 10°C? Assume all thermal energy produced by friction is absorbed by the block. (Take c_{iron}= 450 J/kg°C)

27. **Joule's experiment.**



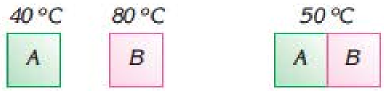
Joule used energy produced by falling weights to increase the temperature of a certain amount of water.

Considering Joule's apparatus, shown in the figure, what is the change in the temperature of the water, when the weight (m = 5.0 kg) is released 10 times from a height of 1.0 m? The mass of the water in the apparatus is 1.0 kg.

28. A lead bullet moving at 200 m/s strikes and becomes embedded in a wooden wall. By how many degrees does the temperature of the bullet increase, if 60% of the thermal energy produced during the impact is absorbed by the bullet? The specific heat of lead is 130 J/kg °C.

4.6 Calorimetry

29.



Two objects, made of different materials, have equal masses. The initial temperatures of the objects are 40 °C and 80 °C. When the two objects are placed in contact, their final temperature is 50 °C.

What is the ratio of the specific heats $\frac{c_A}{c_B}$ (Assume no heat loss to the surroundings)

30. How many grams of water at 25 °C must be added to 300 g of water at 40 °C, for the final temperature to be 30 °C? (No heat is lost to the surroundings.)

31. 200 g of ethanol at 90 °C is mixed with 100 g of water at 10 °C. What is the final temperature of the mixture? (Take $c_{ethanol}$=0.6 cal/g °C)

32. 300 g aluminum at 500 °C is dropped into 2 kg water at 10 °C. What is the final temperature? (Take c_{Al}=0.2 cal/g °C)

33. A 300-g piece of hot metal, at 400 °C, is dropped into 1 kg of water at 20 °C, contained in a 500 g aluminum can.

What is the specific heat of the dropped metal, if the final temperature is 30 °C? (Take c_{Al}=0.2 cal/g °C)

4.7 Phase Change

(Take c_{ice} = 0.5 cal/gr °C, L_f(ice) = 80 cal/gr = 335 kJ/kg, L_v(water) = 540 cal/gr = 2 260 kJ/kg)

34. What is the definition of latent heat of fusion?

35. What is the definition of latent heat of vapourisation?

36. We know temperature stays constant during melting and boiling. From a molecular point of view, what happens to the heat energy absorbed by the substance during phase change?

37. How can we explain the fact that vapourisation latent heats of substances are much greater than fusion latent heats, from a molecular point of view?

38. Why does cologne feel cool when it evaporates from our skin?

39. Why is the weather generally warm while it is snowing?

40. What factors affect the melting point of a substance?

41. Is the internal energy of 1 kg of ice at 0 °C equal to 1 kg of water at 0 °C?

42. An ice block having of mass 200 g floats over 1 kg of water. 100 cal heat energy is transferred to the water. What is the final temperature of the water?

43. How much heat is needed to melt 10 g of aluminum at 660 °C (L_f = 397 kJ/kg)?

44. What amount of heat energy is needed to convert 50 g ice at - 10 °C to water at 30 °C?

45. How many kilojoules of energy is needed to completely vapourise 100 g of water, initially at 50°C?

46. A 2000-W electric heater is immersed in water at 100 °C. Determine the time rate of vapourisation of water.

47. A 1000-W electric kettle contains 1 200 g of water at 25 °C. In how many minutes, after the power is switched on, is 200 g of water left in the kettle?

48. Calculate the amount of water vapourising from the human body in 1 hour. Assume that the human body generates thermal energy at a rate of 100 W and the body temperature is kept constant, mainly by perspiration.

49. What is the minimum velocity of a lead bullet if it completely melts when it strikes a wall? The initial temperature of the bullet is 127 °C and the melting point of lead is 327 °C.

Assume all the thermal energy produced by the impact is absorbed by the bullet.

(Take c_{lead}=128 J/kg °C, L_f=23 kJ/kg)

50. Two identical pieces of ice at –20 °C fly towards each other with equal velocities. Both pieces completely melt upon impact. What are the minimum possible velocities of the pieces before the impact?

51. 20 g of molten lead at its melting point (327 °C) is poured onto 10 kg of ice at 0 °C. How much ice will melt? (Take c_{lead}=128 J/kg °C, L_f(lead)=23 kJ/kg)

52. 40 g ice at –10 °C is placed into a container of water at 0 °C. How many grams of water changes into ice? (The container is thermally insulated)

53. An unknown amount of water at 70 °C is poured onto 10 g of ice at a temperature of 0 °C. What is the mass of water, if the final temperature is 20 °C? (Heat exchange takes place only between ice and water.)

54. A calorimeter contains 100 g water and 40 g ice in thermal equilibrium. The heat capacity of the calorimeter itself is 30 cal/°C. A piece of hot iron at 150 °C is dropped into the water in the calorimeter. What is the mass of the iron piece, if the equilibrium temperature in the calorimeter becomes 10°C? (Take $c_{iron}=0.1 cal/g.°C$)

55. An electric heater increases the temperature of a definite amount of water from 10 °C to 100 °C in 10 minutes. How long will it take the water to boil away completely?

4.8 Heat of Combustion (q)

56. Burning 15 g of gasoline produces 690 kJ of heat energy. What is the heat of combustion for gasoline in units of MJ/kg? (MJ=MegaJoules)

57. How many kilograms of coal is needed to increase the temperature of 2 tons of water from 20 °C to 90°C? The heat of combustion for coal is 29 MJ/kg.

58. 8 g of alcohol is burned while heating 200 gr of water from 20°C to 80°C on a Bunsen burner. What percent of the heat from the combustion of alcohol is used in heating the water? (Take $q_{alcohol}$= 30 MJ/kg)

4.9 Heat Transfer

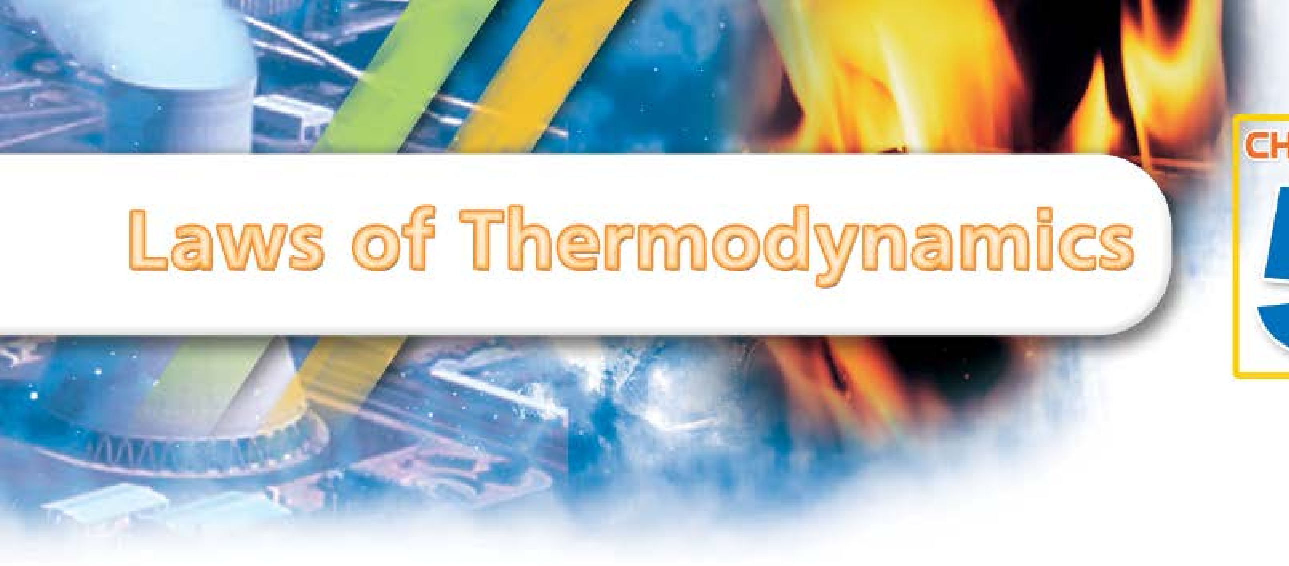
59. Which factors affect the rate of heat transfer in the process of conduction?

60. Which type of heat transfer does not require a material medium?

61. Why are the hot surfaces of a toaster painted black?

62. Why is the inside surface of a thermos bottle made shiny?

63. A 3000 W heater keeps a houses temperature at 20 °C, when the outside temperature is 10 °C. What should the power of the heater be to keep the house at the same temperature, when the outside temperature drops to zero?



Laws of Thermodynamics

CHAPTER

5

Thermodynamics is the study of energy and energy conversion. The laws of thermodynamics emerged in the mid-nineteenth century, when heat was understood to be a form of energy transfer. The first law of thermodynamics is an expression of the conservation of energy, identifying heat and work as two methods of transferring energy. The second law of thermodynamics determines the direction of energy flow and describes the usefulness of energy, showing that it is a quantity different from amount of energy. Heating all the water in a lake from 20 °C to 21 °C requires billions of calories. However, it is not possible to use the tremendous amount of thermal energy in the lake to boil an egg. All we need is a glass of water at 100 °C.

Thermodynamics deals with macroscopic properties such as pressure, volume, heat, work, and internal energy. As discussed in previous chapters, macroscopic properties can be described in terms of molecules. For example pressure and temperature involve the average effects of billions of molecules. However, the laws of thermodynamics were settled before the molecular structure of matter was fully realised. Classical thermodynamics does not make reference to molecules. Nevertheless, in this chapter, we will continue to explain thermodynamical principles in terms of the motion of molecules, in order to attain a better understanding of them.

5.1 DEFINITIONS

System and Surroundings

A **system** is a definite group of objects or substances. What is included in the system and what is outside the system must be well specified. Everything out of the system boundary is called the **surroundings** of the system.

The system chosen can be as simple as a glass of water, a piece of iron, or a gas sample in a cylinder - piston mechanism. On the other hand, a human body can be chosen as a system, although it is infinitely more complex than a gas sample.

The choice of system in thermodynamics is arbitrary. However, clearly defining the system boundary is very important. Consider a gas trapped in a vertical cylinder by a movable piston. The initially fixed piston is allowed to fall freely, but is stopped by the increasing gas pressure. To analyse the situation two different systems can be chosen:

a) The gas in the cylinder shown in Figure 5.1a

In this case: 'the energy of the system has increased', because potential energy lost by the falling piston (which is outside our system), is transferred to the gas.

b) The gas and the cylinder - piston mechanism shown in Figure 5.1b.

In this case: 'the energy of the system has not changed', because the energy lost by one part of the system is gained by another part.

A closed system means there is no matter transfer between the system and its surroundings. For an isolated system neither matter nor energy is transferred between the system and surroundings. An open system allows both matter and energy transfers, as shown in Figure 5.2

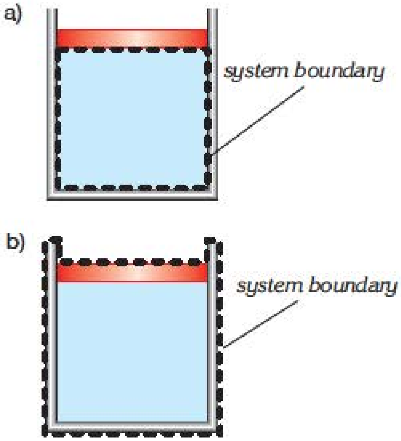


Figure 5.1 a) A 'system' consists of the gas only. b) The 'system' consists of the gas and the cylinder-piston mechanism

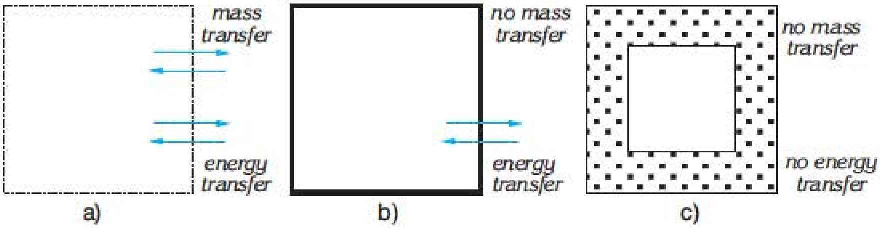


Figure 5.2 Three types of system a) Open system b) Closed system c) Isolated system

State of a System

Any characteristic of a system is a system property. The state of a system is described by a set of properties. To describe a state, the properties that completely describe the exact condition of a system must be chosen.

To specify the state of a person, many variables are required: weight, height, intelligence, looks, fitness, economic situation.

A gas sample, on the other hand, is a much simpler system. Three variables: pressure, volume and temperature are enough to describe the exact condition of a gas sample. A specified set of values of P, V and T is called the state of a gas.

State variables are the variables which have the same value when the system is in a given state. Pressure, volume and temperature are state variables for a gas. Internal energy is also a state variable as discussed in this chapter.

An equilibrium state of a gas means that temperature (hence pressure and density) of the gas sample has the same value throughout the volume. When a gas sample is in equilibrium, microscopic parameters - such as speed of a certain molecule-changes in time. However, macroscopic parameters, involving average effects of countless molecules (such as pressure and temperature) remain constant in time.

When a gas sample is in equilibrium, there are definite values of P and T. In other words, pressure or temperature of a gas has well defined values only when the gas sample is in an equilibrium state.

Thermodynamics deals with systems in equilibrium states. Non-equilibrium situations are not the subject of classical thermodynamics.

Thermal Processes

A change from one state to another is called a process. In this chapter slow processes will mainly be considered. A slow process is easy to analyse.

Consider a gas in a cylinder-piston system being compressed to half its original volume. Two different courses of action can be taken:

Pressure can be increased very slowly, for example by dropping extremely small masses, such as grains of sand on the piston. This process is shown in Figure 5.3. Since the process is very slow, the gas stays nearly homogeneous and passes through a series of equilibrium states. At every state there is a definite value for pressure, temperature and volume. Such a slow process is called quasi-static.

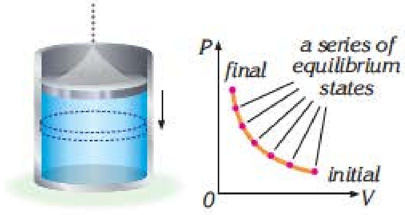


Figure 5.3 The pressure is increased slowly by dropping sand grains on the top of the piston

Another option is to drop a brick on the piston. In this case initial and final states can still be determined, but pressure and temperature are not well defined during the intermediate steps, since the gas is turbulent, as shown in Figure 5.4.

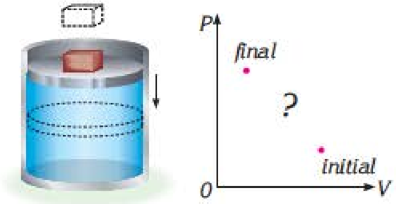


Figure 5.4 Pressure is increased suddenly by dropping a brick on the top of the piston.

5.2 INTERNAL ENERGY OF A GAS

Chapter 2 discussed how gas molecules have only kinetic energy. Therefore,

$$\begin{matrix}\text{Internal energy of}\\ \text{a gas sample}\end{matrix} = \begin{matrix}\text{Number of}\\ \text{molecules}\end{matrix} \times \begin{matrix}\text{Average kinetic energy}\\ \text{of one molecule}\end{matrix}$$

Since the temperature of an ideal gas indicates the average kinetic energy of gas molecules

$$\begin{matrix}\text{Internal energy of}\\ \text{a gas sample}\end{matrix} \sim \begin{matrix}\text{Number of}\\ \text{molecules}\end{matrix} \times \text{Temperature}$$

Therefore the internal energy formula for a gas is expected to have the form

$$U_{gas} = (\text{const}) \times N \times T$$

This constant will be calculated for simple gases in chapter 6.

The internal energy of a gas is a function of temperature. In other words, the internal energy of a gas cannot be changed without changing its temperature.

$$\left.\begin{matrix}\Delta T > 0 & \longleftrightarrow & \Delta U > 0\\ \Delta T < 0 & \longleftrightarrow & \Delta U < 0\\ \Delta T = 0 & \longleftrightarrow & \Delta U = 0\end{matrix}\right\}\text{for gases}$$

Such a direct relationship cannot be written for solids or liquids, since the internal energy of solids or liquids may change while the temperature remains constant; as is the case during a phase change.

5.3 TRANSFERRING ENERGY TO A SYSTEM

It is possible to transfer energy to a system in two ways. Mechanically, by doing work on a system increases its energy. In the previous chapter heat was defined as a form of energy transfer due to temperature difference.

Consider the system to be a gas sample trapped in a cylinder by a movable piston. Energy can be transferred to the gas in two ways, as shown in figure 5.5

- The piston can be pushed down, doing work on the system
- The gas can be heated

In both cases the energy supplied from the surroundings will be added to the internal energy of the gas. Since internal energy of a gas is proportional to its temperature, both processes will make the gas sample hotter.

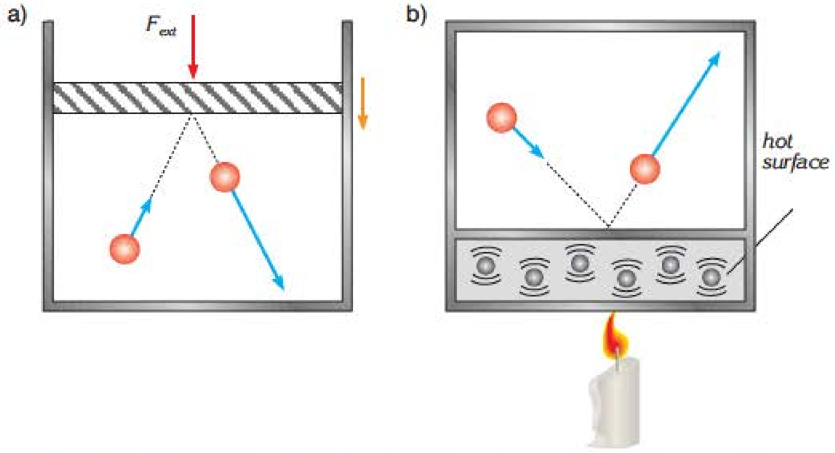


Figure 5.5 Two ways of transferring energy to a system a) External work done on the system increases internal energy b) 'Heating' increases internal energy

Mechanical work is defined as energy transfer to or from a system, not due to a temperature difference.

From a molecular point of view, work done by an external force increases the internal energy of the gas, because molecules bounce back faster from a collision with the moving piston. This process is similar to a ping-pong ball being struck by a moving racquet. Heating also increases the speed of gas molecules, as they interact with 'hot' molecules of the walls, along with the radiation they absorb.

Work Done on a System and Work Done by a System

Consider a gas in a frictionless cylinder-piston system slowly being heated, as shown in Figure 5.6. Increasing the temperature causes the piston to move upwards. By Newton's third law, when the gas exerts a force $\vec{F}$ on the piston, the piston exerts a force $-\vec{F}$ on the gas. The forces are equal in magnitude but opposite in direction. Therefore when one of them does positive work, the other does negative work of an equal amount.

$$W_{\text{by the gas}} = -W_{\text{on gas by the external forces}}$$

- If the gas is expanding, $W_{\text{by gas}}$ is positive W_{external} is negative
- If the gas is compressed, $W_{\text{by gas}}$ is negative W_{external} is positive

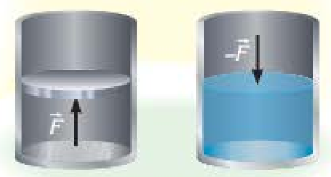


Figure 5.6 The two forces constitute an action-reaction pair

5.4 THE FIRST LAW OF THERMODYNAMICS

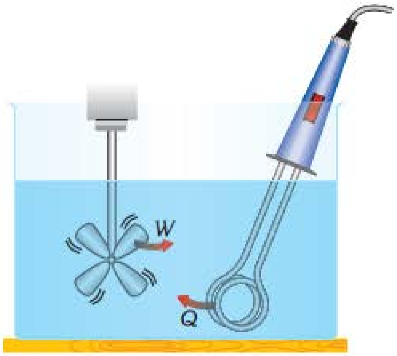


Figure 5.7 The internal energy (and hence temperature) of water can be increased in two ways: by transferring heat to water or by doing work on the water

Two methods of transferring energy to or from a system are heat and work, as shown in Figure 5.7. Using the conservation of energy

$$\text{Increase in internal energy} = \text{Heat added to the system} + \text{Work done on the system}$$

Written in symbols

$$\Delta U = Q + W_{\text{on the system by external forces}}$$

The expression above is the first law of thermodynamics.

Question

Question: Can the first law of thermodynamics be derived with a different line of reasoning, using work done by the system, rather than external work?

Answer

As discussed earlier the first law of thermodynamics is simply the law of conservation of energy. The first law of thermodynamics can be justified as follows:

Consider a gas sample being slowly heated in a cylinder-piston system, as shown in Figure 5.8. Heat absorbed by the system can be used in two ways:

- The gas can lift the piston, doing mechanical work.
- The absorbed heat energy can be stored in the gas, increasing its internal energy.

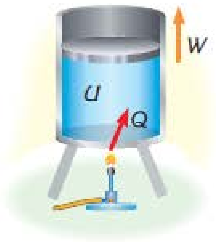


Figure 5.8 Heat absorbed by a gas is used to do work and increase the internal energy

Since energy is conserved

$$\text{Heat given to a system} = \text{Increase in internal energy} + \text{Work done by the system}$$

$$Q = \Delta U + W_{\text{by system}}$$

Once again this is the first law of thermodynamics, yet with a different emphasis.

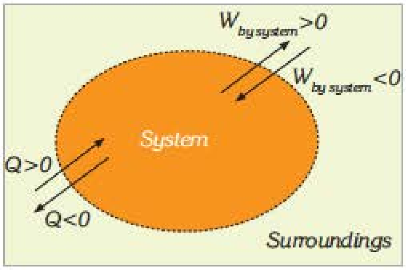


Figure 5.9 The sign convention for heat and work

All terms in the expression can be positive or negative as shown in Figure 5.9. Consider the gas sample in Figure 5.8. In the system:

- ΔU is positive if internal energy increases. (Temperature increases).
- ΔU is negative if internal energy decreases. (Temperature decreases).
- Q is positive, if heat is added to the system.
- Q is negative, if heat flows out of the system.
- $W_{\text{by gas}}$ is positive, if work is done by the gas, lifting the piston and hence increasing the volume
- $W_{\text{by gas}}$ is negative, if work is done on the gas, decreasing the volume.

Example 5.1 Using the first law of thermodynamics

A system does 300 J of work as it absorbs 800 J heat. What is the internal energy change of the system?

Solution

Q is positive since the system absorbs heat energy from the surroundings

Thus, $Q = +800$ J.

Since the system itself does work, W done by the system is also positive,

$W_{\text{by system}} = +300$ J

Using the first law,

$Q = \Delta U + W_{\text{by the system}}$

$\Delta U = Q - W_{\text{by the system}}$

$\Delta U = (+800 \text{ J}) - (+300 \text{ J})$

$\Delta U = +500$ J

The internal energy of the system has increased by 500 J, as shown in Figure 5.10.

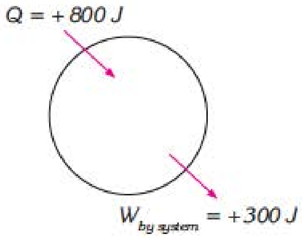


Figure 5.10 The graphical representation of the solution

Example 5.2 Increasing internal energy by doing work

640 J work is done on a gas in a cylinder-piston system, and of 200 J heat is released. Find the change in the internal energy of the gas.

Solution

Work done on the gas by an external force equals + 640 J. This amount of work increases the internal energy of the gas by 640 J.

$W_{\text{external}} = +640$ J

Since the gas releases heat

$Q = -200$ J.

Using the first law

$\Delta U = Q + W_{\text{external}}$

$\Delta U = (-200 \text{ J}) + (+640 \text{ J})$

$\Delta U = +440$ J

The internal energy of the system has increased by 440 J.

Example 5.3 Comparing isovolumetric and isobaric processes

The same amount of heat is absorbed by two identical samples of gas, one kept in a closed container, the other in a cylinder under a movable piston.

Do the two gas samples undergo the same temperature change, since they absorb the same amount of heat?

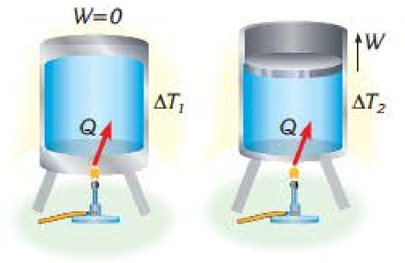


Figure 5.11 The gas becomes hotter in the first case, as all the heat is used in increasing the temperature

Solution

In the first case all the heat energy is converted into internal energy of the gas. In other words, all the heat is used to make the gas hotter.

In the second case, however, heat added to the system is used for two purposes:

- Increasing the internal energy, making the gas hotter.
- Doing work on the piston, lifting it up, and hence increasing its potential energy.

Therefore the gas in the closed container will be hotter, when both systems absorb the same amount of heat, as shown in Figure 5.11.

5.5 WORK IN A THERMODYNAMIC PROCESS

An expression can be derived, during a slow thermal process, to calculate the work done by a gas.

Consider the gas sample in Figure 5.12, expanding against a movable piston. A movable piston keeps the pressure constant. Work done by the gas is given by

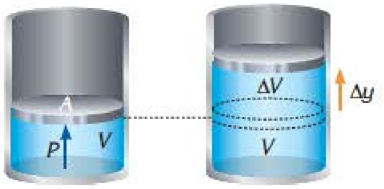


Figure 5.12 The gas sample does work, as it pushes the piston upwards, increasing its volume.

$$\text{Work} = \text{Force x distance}$$

$$W_{\text{by gas}} = F_{\text{by gas}} \times \Delta y$$

$$W_{\text{by gas}} = (P_{\text{gas}} \times A) \times \Delta y$$

$$W_{\text{by gas}} = P_{\text{gas}} \times (A \times \Delta y)$$

$$W_{\text{by gas}} = P_{\text{gas}} \times \Delta V$$

In general,

$$W = P\Delta V \quad (P = \text{const})$$

The unit of the product (PΔV) can be found

$$[\text{Pa}]\times[\text{m}^3] = \left[\frac{\text{N}}{\text{m}^2}\right]\times[\text{m}^3] = [\text{N}\cdot\text{m}] = [\text{J}] \text{ as we expected.}$$

The formula indicates that

- Increase in volume $\longleftrightarrow$ $\Delta V > 0$ $\longleftrightarrow$ $W_{\text{by gas}} > 0$
- Decrease in volume $\longleftrightarrow$ $\Delta V < 0$ $\longleftrightarrow$ $W_{\text{by gas}} < 0$
- Constant volume $\longleftrightarrow$ $\Delta V = 0$ $\longleftrightarrow$ $W_{\text{by gas}} = 0$

as discussed earlier.

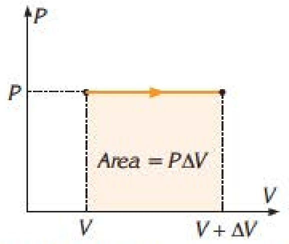


Figure 5.13 (Height × base) of the shaded area is (P × ΔV)

Finding Work from the P - V Graph

The pressure-volume graph in Figure 5.13 shows volume expansion under constant pressure.

Examining the P-V graph in Figure 5.13, the following conclusion is reached:

Area under the curve of the P - V graph equals the magnitude of the work done

This conclusion is always correct, although it was reached using the simple constant pressure case, as shown in Figure 5.14.

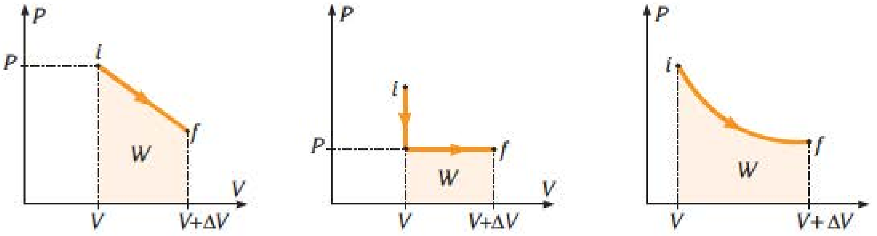


Figure 5.14 The area under the P-V curve equals the magnitude of the work in all

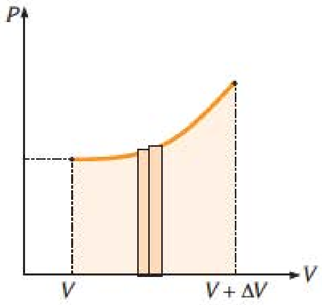


Figure 5.15 Total area is the sum of the rectangular strips

Even if the pressure changes, the curve under the P-V graph can be divided into small, constant pressure steps. The total area under the curve can be considered as the sum of small rectangular areas, this is shown in Figure 5.15. As thinner and thinner rectangles are used, the error in calculation becomes smaller.

Example 5.4 Work done during expansion

A gas sample expands from 3 lt to 8 lt against standard atmospheric pressure. What is the work done by the gas?

Solution

As the pressure is constant, the PΔV formula can be used.

To find the result in joules, we can use the SI units of Pascals and m^3 must be used.

$$P = 1 \text{ atm} \approx 10^5 \text{ Pa}$$

$$\Delta V = V_f - V_i = 8 \text{ lt} - 5 \text{ lt}$$

$$\Delta V = 3 \text{ lt} = 3 \times 10^{-3} \text{ m}^3.$$

$$W = P\Delta V$$

$$W = (10^5 \text{ Pa})(3 \times 10^{-3} \text{ m}^3)$$

$$W = 300 \text{ J}$$

Work done by the gas is positive, since the gas is expanding.

Example 5.5 Work done during an isobaric process

0.2 moles of an ideal gas is heated from 300 K to 400 K under constant pressure. What is the work done by the gas?

Solution

Since the pressure is constant, the PΔV formula can be used. However, neither pressure nor volume change are given in the question. Though the PΔV product can be calculated from given values, it will be easier to use a different approach.

Writing down the ideal gas law for initial and final states,

$$\begin{aligned} PV_2 &= nRT_2 \\ -\ PV_1 &= nRT_1 \\ \hline P\,(V_2 - V_1) &= nR\,(T_2 - T_1) \\ P\Delta V &= nR\Delta T \\ \boxed{W = nR\Delta T} &\quad (P = \text{const}) \end{aligned}$$

Now there is a new formula to calculate work done under constant pressure.

Substituting the numbers,

$$W_{\text{by gas}} = (0.2) \times (8.31\ \text{J/K}) \times (100\ \text{K})$$

$$W = 166.2\ \text{J}$$

Example 5.6 Getting hotter while giving out heat

A gas sample is compressed along the i - f curve, as shown on the P - V graph in Figure 5.16. During compression, the internal energy of the gas increases by 40 J.

What is the amount of heat energy transferred to the gas during compression?

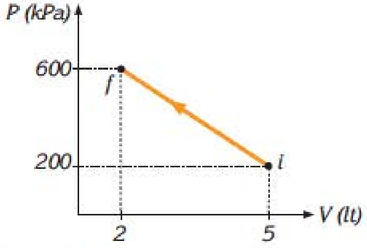


Figure 5.16 The gas is compressed from state (i) to state (f) along the curve shown on the graph

Solution

The internal energy change of the system is given in the question. To find the heat, all that is needed is the work done by the system.

The magnitude of work equals the area under the P - V graph, as shown in Figure 5.17.

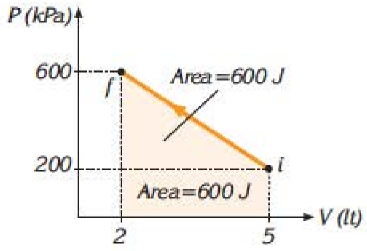


Figure 5.17 The gas is contracting. Work done by the gas is –1200 J.

Area = 1200 J.

Since volume is decreasing, the work done by the gas is negative.

$$W_{\text{by gas}} = -1200\ \text{J}$$

To find the amount of heat transferred, the first law of thermodynamics is used

$$Q = \Delta U + W_{\text{by gas}}$$

$$Q = (+40\ \text{J}) + (-1200\ \text{J})$$

$$Q = -1160\ \text{J}$$

It is interesting to note that, while the increasing internal energy indicates a rising temperature, a negative heat value indicates that the gas releases heat.

In other words, the gas gets hotter as it loses heat. The surroundings are colder than the gas.

The required energy for both (heating the gas and losing heat to the environment) is supplied by the work done on the gas, as shown in Figure 5.18.

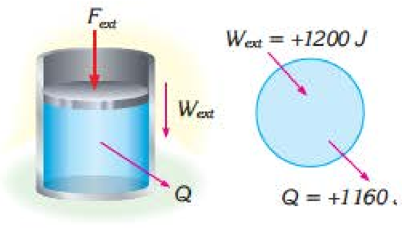


Figure 5.18 The gas releases heat but its temperature increases.

Example 5.6 showed that increase in temperature does not necessarily imply absorbing heat energy. Temperature may increase even when the system gives out heat.

Absorbing heat does not necessarily result in an increase in temperature. Conversely, losing heat energy does not necessarily mean a decrease in temperature.

Therefore the words 'heating' and 'cooling' should be avoided in a scientific context. This is because the phrase 'heating a gas sample' may have two meanings: 'transferring heat to the gas' or 'increasing the temperature of the gas'.

5.6 STATE VARIABLES AND PATH DEPENDENT VARIABLES

For a fixed amount of gas, the temperature can be found, if the pressure and volume of the gas is known.

A point on a P-V graph indicates definite values of pressure and volume. Therefore every point on the P-V graph has a definite temperature for a fixed amount of gas.

Points on a P-V graph are called 'states', as they represent definite values of P, V and T, as shown in Figure 5.19.

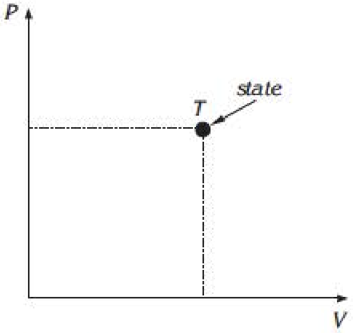


Figure 5.19 Every point on the P-V graph represents a state

Pressure, volume and temperature are called 'state variables'.

Internal energy is also a state variable. Internal energy of a gas sample is a function of temperature only. For a definite amount of gas, every specific temperature value corresponds to a specific amount of internal energy. Therefore for a given state, the internal energy of a gas has a fixed value. When the gas sample is returned to this state, its internal energy returns to the same value.

State variables are macroscopic parameters. For a given state, a gas sample has fixed values of P, V, T and U. However, speed or energy of a given molecule changes. The values of state variables are determined by the average effects of billions of molecules.

Heat and work are not state variables. Heat or work contained in a system cannot be referred to. Internal energy is a property of a system. Heat and work are not properties of a system, in a given state, but variables of the process between two states.

Consider two different processes between two fixed states, as shown in Figure 5.20. Along process (1), the gas expands at constant pressure.

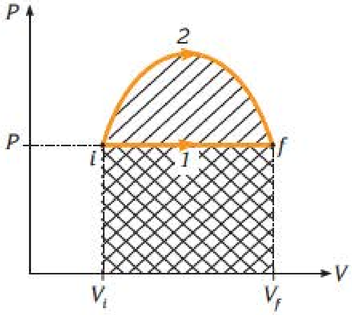


Figure 5.20 Gas expands from state (i) to state (f) along two different paths. During which process does it absorb more heat?

Along process (2), the gas expands from the same initial state to the same final state as process (1), but during the process, pressure is first increased, then decreased to the original value, by placing and removing weights on the piston.

Comparing ΔU, W and Q during the two processes:

- Since T_i and T_f have fixed values at states 'i' and 'f', regardless of the intermediate steps, $\Delta T_1 = \Delta T_2$. Since equal temperature change indicates equal internal energy change for a gas sample

$$\Delta U_1 = \Delta U_2$$

- Comparing the areas under the curves

$$W_2 > W_1$$

- Using the first law of thermodynamics, $Q = \Delta U + W$

$$Q_2 > Q_1$$

Although the initial and final states are the same, the gas absorbs more heat along path (2), since it does more work along this path.

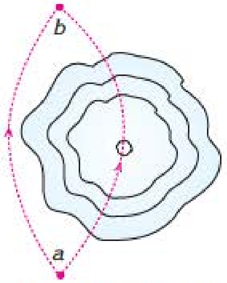


Figure 5.21 Two different routes connecting two villages

This is analogous to walking from one village to another, along two different paths: one passing over a hill, the other along a level plain, as shown in Figure 5.21. Both paths take us from village (a) to village (b), but one requires much more energy than the other.

Heat and work depend not only on the initial and final states, but also on the intermediate states in-between.

Thus, heat and work are not state variables, because they depend on the path between the initial and final states. Such variables are called 'path-dependent'.

5.7 THERMAL PROCESSES

Some particular thermal processes and their characteristic properties, will now be analysed. Adiabatic processes, isothermal processes, isovolumetric processes and cyclic processes will be discussed in reference to the first law of thermodynamics.

An **adiabatic process** is defined as a process during which a system does not exchange heat with the surroundings.

During an adiabatic process $Q = 0$.

An adiabatic process can be achieved by two different methods.

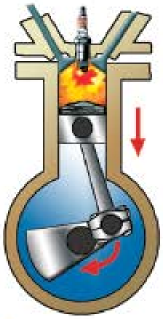


Figure 5.22 A sudden expansion does not leave time for heat transfer. The process is adiabatic.

If the process is fast enough, so as to not to leave time for heat exchange with the surroundings, the process is adiabatic. Sudden compression of a gas in a cylinder, or the sudden explosion of a gas-air mixture in a car motor are examples of an adiabatic process, as shown in Figure 5.22.

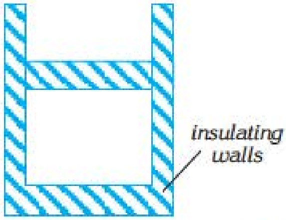


Figure 5.23 A process is adiabatic when the system is isolated

A process occurring in an isolated system is also adiabatic. An isolated system is typically the cylinder-piston apparatus with insulating walls, as shown in Figure 5.23.

An adiabatic process should not be confused with an isothermal process. Preventing heat exchange does not mean that the temperature remains constant. If a gas sample is compressed adiabatically, its temperature increases. Although no heat is transferred, work done on the gas increases its internal energy. If, on the other hand, a gas sample expands adiabatically, its temperature decreases, as it uses its own internal energy to do work.

During a slow adiabatic expansion, a gas sample follows a path similar to the one shown in the P-V graph of Figure 5.24. For comparison, two constant temperature curves are also shown on the same graph. It can be seen that the temperature of the gas decreases during an adiabatic expansion.

Let us apply the first law of thermodynamics for an adiabatic process. Since Q= 0, the equation is

$$\Delta U = -W_{\text{by system}} \text{ (adiabatic process)}$$

This equation can be interpreted in two ways:

- $\Delta U = W_{\text{on system}} \longrightarrow$ Work done on the system is used only for increasing the internal energy of the system.
- $W_{\text{by system}} = -\Delta U \longrightarrow$ The system does work using its own internal energy.

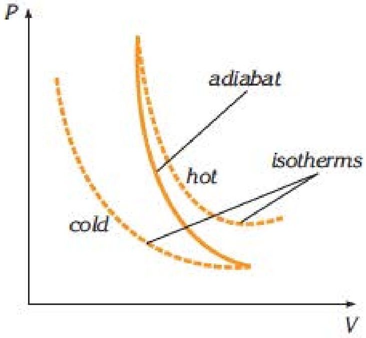


Figure 5.24 P-V graphs showing adiabatic curves and isotherms

An **isothermal process** is defined as a process which occurs at constant temperature.

For a fixed amount of ideal gas, internal energy is a function of temperature only. Therefore, for an ideal gas sample, constant temperature implies constant internal energy. Thus

$$T = \text{constant} \longleftrightarrow U = \text{constant} \longleftrightarrow \Delta U = 0$$

for an ideal gas. The first law of thermodynamics becomes

$$Q = W \text{ (isothermal process)}$$

The equation indicates that the gas sample uses all the heat energy absorbed from the surroundings to do work on the surroundings. So, the internal energy of the gas does not change.

An **isovolumetric process** is defined as a process occurring at constant volume. Since a system does not do work at constant volume

$$V = \text{constant} \longleftrightarrow \Delta V = 0 \longleftrightarrow W = 0$$

The first law of thermodynamics is

$$Q = \Delta U \text{ (isovolumetric process)}$$

In other words, the system uses all the heat energy absorbed to increase its internal energy.

Example 5.7 An adiabatic expansion

A gas expands adiabatically by doing 60 J work in an expansion. What is the internal energy change of the gas?

Solution

Since the expansion is adiabatic, Q = 0.

thus, $\Delta U = -W_{\text{by gas}}$

$\Delta U = -60\text{ J}$

The internal energy of gas has decreased by 60 J.

Example 5.8 Isothermal compression

A gas is isothermally compressed to half of its original volume. During the process 30 J of heat flows out of the gas. What is the work done by the gas?

Solution

The isothermal process implies constant internal energy for a gas. Since the heat flows out of the gas Q= –30 J.

$$\Delta U = 0$$
$$Q = W_{by\ gas}$$
$$W_{by\ gas} = -30\ J$$

Since the gas is compressed by an external force, work done by the gas is negative.

Example 5.9 An isovolumetric process

The temperature of a 500 g iron cube increases from 20 °C to 200 °C, as it absorbs heat under atmospheric pressure. What is the internal energy change of the iron cube? (Take $c_{iron} = 460$ J/kg.°C)

Solution

Actually the volume of iron increases with temperature, due to thermal expansion. So the iron cube does work by pushing against the atmosphere. But since the volume change is very small, the process can be approximated as being isovolumetric.

$$\Delta V = 0$$
$$W = 0$$
$$\Delta U = Q$$
$$\Delta U = mc\Delta T$$
$$\Delta U = (0.5\ kg)(460\ J/kg\ °C)(180\ °C)$$
$$\Delta U = 41\ 400\ J$$

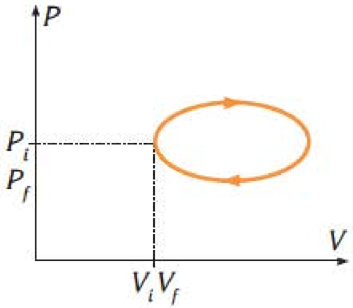


Figure 5.25 A cyclic process

Cyclic processes will prove to be very important in the study of heat engines. A cyclic process takes a gas sample back to its initial state after passing through many intermediate states.

Consider the cyclic process undergone by a gas sample, as displayed in Figure 5.25. When the gas returns to its initial state; pressure, volume and temperature take their initial values.

$$P_f = P_i,\ V_f = V_i,\ T_f = T_i$$

Since initial and final temperatures are equal, the initial and final internal energies of the gas are also equal. Therefore the net change in internal energy is zero.

$$T_f = T_i \xleftrightarrow[\text{for gases}]{} U_f = U_i \leftrightarrow \Delta U_{complete\ cycle} = 0$$

The internal energy of the gas is not constant during the process. Along the cyclic curve on the P-V graph, temperature and internal energy of the gas may increase or decrease. However, when the gas returns to its initial state, the internal energy returns to its initial value. The net change in internal energy becomes zero.

The first law of thermodynamics applied to a complete cycle is

$$Q_{\text{complete cycle}} = W_{\text{complete cycle}}$$

Work Done in a Cyclic Process

Consider the cyclic process in figure 5.26. A gas sample first expands from state 1 to state 2 along the upper curve, and then it is once again compressed to state 1 along the lower curve.

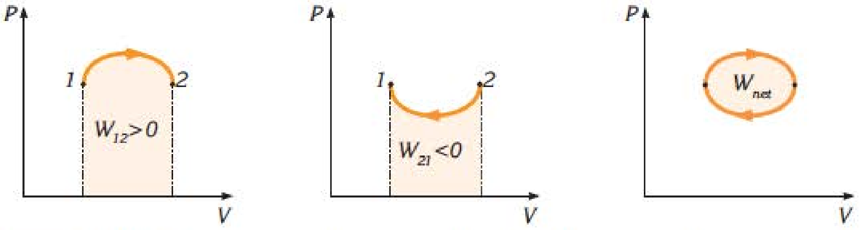


Figure 5.26 Work done in a cyclic process. How does the sense of rotation affect the sign of the net work done by the gas?

Work done by the gas when it changes from state 1 to state 2 is positive. Work done by the gas when it changes from state 2 to state 1 is negative. Net work done in one cycle is given by

$$W_{\text{complete cycle}} = W_{12} + W_{21} = \text{Area of cycle}$$

Therefore, the net work done by the gas in one complete cycle equals the area inside the cycle.

Example 5.10 Heat in a cyclic process

A sample of an ideal gas undergoes the cyclic process shown in Figure 5.27. What is the thermal energy transferred to the gas in one cycle?

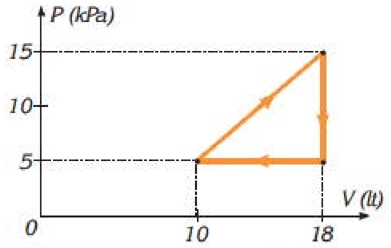


Figure 5.27 The area inside the cycle equals the net work done by the gas

Solution

To find the work done by the gas in one cycle, the area inside the cycle must be calculated.

$$\text{Area} = \frac{(10\times10^{3}\text{Pa})\times(8\times10^{-3}\text{m}^{3})}{2} = 40\text{J}$$

$$W_{\text{by gas}} = 40\text{ J}$$

Work is positive, as the cycle is clockwise. Since the process is cyclic,

$$Q_{\text{complete cycle}} = W_{\text{complete cycle}}$$

$$Q_{\text{net}} = 40\text{ J}$$

The gas absorbs 40 J net heat during one complete cycle.

5.8 HEAT ENGINES

Converting mechanical energy into thermal energy is easy. This can be done by rubbing your hands together or pushing a book over a table. When the book is stopped by the friction force, all the initial kinetic energy will have turned into thermal energy, raising the temperature of the book and the table surface, as shown in Figure 5.28. Mechanical energy can be completely converted into thermal energy.

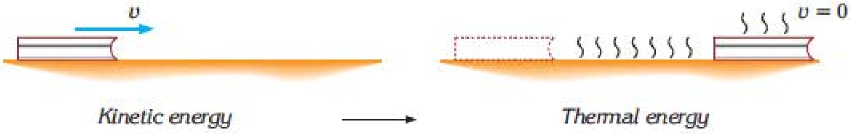


Figure 5.28 Friction converts mechanical energy into thermal energy

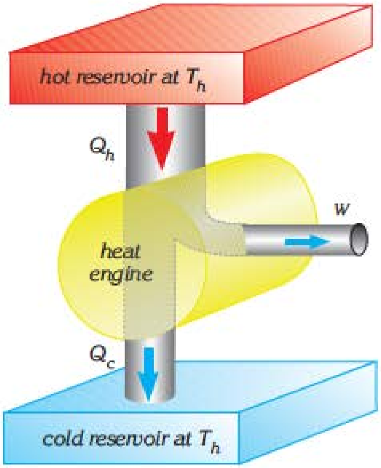


Figure 5.29 Schematic representation of a heat engine

Converting thermal energy into mechanical energy, on the other hand, is difficult.

A device converting thermal energy into mechanical energy is called a heat engine. Heat engines use heat to do work. Car motors, diesel engines, steam turbines and steam power plants are examples of heat engines*. A heat engine usually uses a high pressure gas to push against a piston.

In general, a heat engine absorbs heat energy from a source at high temperature (called the 'hot reservoir'), converts part of this energy into useful work and expels some heat to a low temperature medium (called the 'cold reservoir' or 'heat sink').

Figure 5.29 outlines the operation of a heat engine. Referring to the figure:

Q_h: Amount of heat supplied to a heat engine from a high temperature source.

Q_c: Amount of heat released to a low temperature heat sink (usually the atmosphere)

T_h: Absolute temperature of hot reservoir

T_c: Absolute temperature of cold reservoir

W: Mechanical work output of the engine

Notice that both Q_h and Q_c are defined as positive quantities. For continuous operation, a heat engine must work in cycles.

Efficiency of a Heat Engine

As with any engine, efficiency is defined as

$$\text{Efficiency} \equiv \frac{\text{Useful output}}{\text{Total input}}$$

efficiency is represented by (η).

For a heat engine, useful energy is the mechanical work output, total energy is the heat Q_h absorbed from the hot reservoir.

---

* Car motors, diesel engines and steam turbines do not exactly fit into the definition of a heat engine. The model we use is better suited for heat engines which use the same fluid; heating and cooling it over and over in a thermodynamic cycle. A steam engine or power plant is a good example for the theoretical discussion here. A car motor, on the other hand, releases exhaust gases after the combustion. Nevertheless, our theoretical model still gives us an idea of the basic principles.

Using the efficiency definition for a heat engine

$$\eta = \frac{W}{Q_h}$$

Conservation of energy requires,

$$W = Q_h - Q_c$$

for a cyclic process. Substituting into the efficiency formula gives

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

Mathematically, the efficiency of a system may take values between zero and one, since Q_c cannot be greater than Q_h.

Zero efficiency ($\eta=0$) means all the heat energy absorbed from the hot reservoir is lost as waste heat at the exhaust, and the engine does not produce any work.

$\eta = 0.4$ means out of 100 kJ of heat energy absorbed from the heat source, 40 kJ is converted into useful work, 60 kJ is lost at the exhaust.

Percent efficiency is given by $\eta \cdot 100$. $\eta = 0.4$ means 40% efficiency.

100% efficiency ($\eta=1$) is physically impossible for reasons that will be explained.

Why Are We Wasting Q_c?

Heat engines are low efficiency devices. The efficiency of a typical car motor is about 25 percent. That is, a car motor converts 25 percent of the chemical energy stored in the gasoline into mechanical work. For diesel engines and gas turbines the efficiency can be as high as 40 percent, and even as high as 60 percent for large steam power plants. Therefore, even the most efficient heat engines waste nearly half of the input energy by heating the atmosphere.

The main reason for the low efficiency of a heat engine is Q_c, heat released at the exhaust or condenser. Is it possible to construct a heat engine with $Q_c=0$?

The answer is *no* unfortunately. This is because an engine cannot complete a cyclic process and continue to operate without rejecting any heat.

Consider a very simple heat engine consisting of a cylinder-piston system, as in figure 5.30. This system will be used to lift an object up, converting heat into potential energy.

Examining Figure 5.30 we see that even at ideal conditions (no friction, no heat loss, weightless piston), out of 100 kJ energy we supply to the system, 80 kJ stays

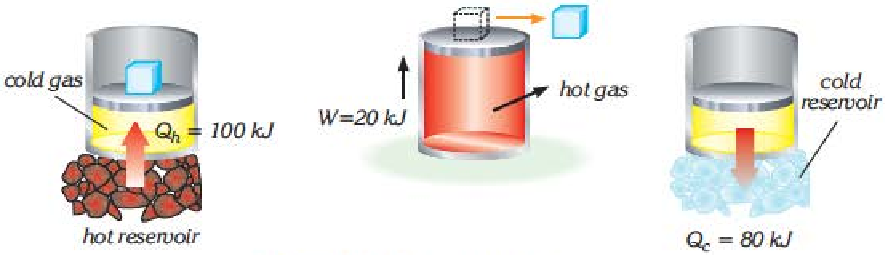


Figure 5.30 A simple heat engine

in the gas, since the temperature of the gas must increase to lift the piston. If our engine is not a single use system (it will continue to operate to lift other objects), the piston must return to its initial height. To do this, the gas must be cooled to its initial temperature. Therefore all the 80 kJ of energy stored in the gas will be wasted, as it is released to a cold reservoir.

Is it possible to transfer this 80 kJ of energy back to the hot reservoir for future use? This would give rise to a super-high-efficiency heat engine. The answer is no again, since heat always flows from a hot place to a cold place. It is impossible to spontaneously transfer heat energy from a hot gas to an even hotter reservoir. The energy stored in the hot gas can only be absorbed by a reservoir at a lower temperature.

This simple analysis shows that the two statements 'heat flows from a hot place to a cold place' and 'a heat engine with 100 percent efficiency cannot be constructed' are equivalent.

Perhaps it is better to construct a heat engine in which the piston moves in a circle instead of moving up and down vertically and causing heat loss.

A steam turbine is such a design. Its construction is shown in Figure 5.31. The high pressure steam from the boiler pushes the blades and rotates the shaft. However, some heat must be lost to cool the steam on the exhaust side. If the temperatures of the steam on both sides of the turbine blades are equal, the turbine simply does not rotate. This is because steam of equal temperature on both sides would apply equal pressures on both sides.

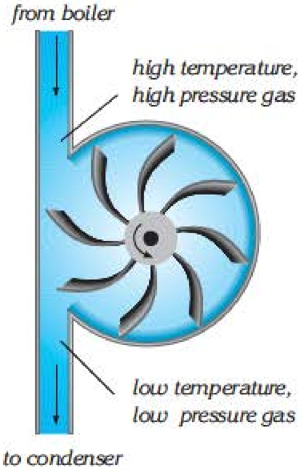

from boiler
high temperature, high pressure gas
low temperature, low pressure gas
to condenser

Figure 5.31 A steam turbine

As a result, even the best designed heat engine, operating under ideal conditions, cannot have 100 percent efficiency, since a temperature difference and heat flow are needed to operate the engine.

5.9 REFRIGERATORS AND AIR CONDITIONERS

Heat does not, by itself, flow from a cold place to a place hot. However, heat from a cold place can be pumped to a hot place by doing work. In a steam turbine, hot gases rotate a turbine, doing work. In a refrigerator work is done on the gas to cool it.

Figure 5.32 is a schematic representation of a refrigerator cycle.

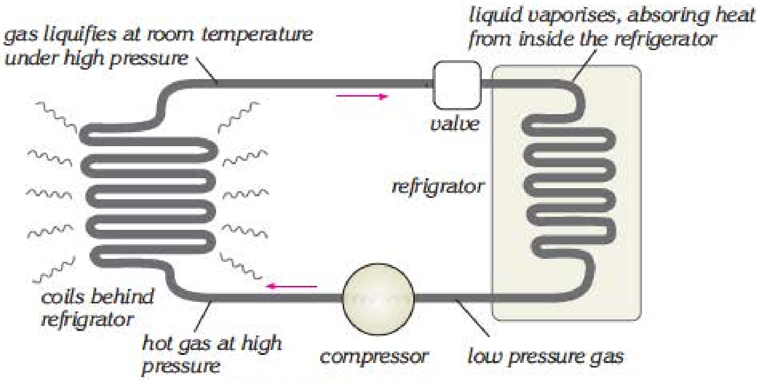

gas liquifies at room temperature under high pressure
liquid vaporises, absoring heat from inside the refrigerator
valve
refrigrator
coils behind refrigrator
hot gas at high pressure
compressor
low pressure gas

Figure 5.32 A refrigerator cycle

A gas is liquefied under high pressure, applied by a compressor. This takes place in the condensation coils, which are outside the refrigerator. The heat given out by the gas (Q_h) as it turns into liquid is transferred to the air in the room.

When the pressure is suddenly released, the liquid vapourises, absorbing the required heat (Q_c) from inside the refrigerator. The gas then enters the compressor and another cycle begins.

Notice that both Q_h and Q_c are defined as positive quantities.

$Q_h > Q_c$ because the heat energy released by the gas, to the room, is not only the heat absorbed from inside the refrigerator; the compressor also transfers energy to the gas during compression. Q_h is the sum of Q_c and work done by the compressor.

$$Q_h = Q_c + W$$

Therefore a refrigerator actually heats more then it cools the kitchen, even if it operates with its door open.

An air conditioner works just like a refrigerator. Only the condensation coils are outside the building and evaporation coils are inside the room. Thus, it pumps the heat from the colder room to the hotter outside by doing work. The net effect is heating the atmosphere, though the room gets temporarily cooler, because the work done by the engine is converted into heat.

Example 5.11 Heat waste from a power plant

Water from a river is used to cool a 500-MW (Megawatts) steam power plant, as shown in Figure 5.33. The thermal efficiency of the plant is 40 percent. What is the rate of heat transfer to the river?

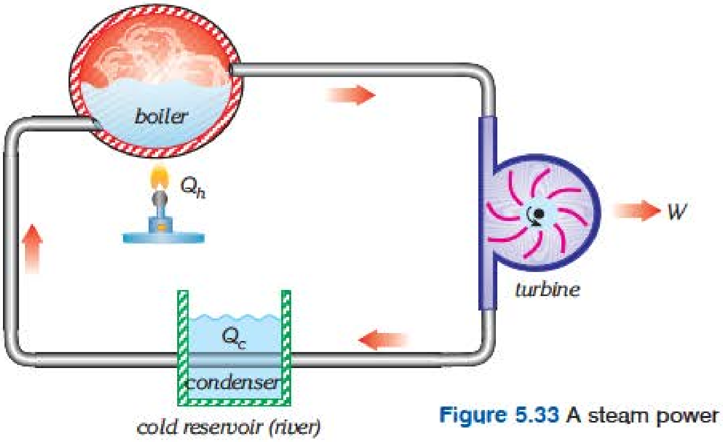


Figure 5.33 A steam power plant

Solution

Remember (Watt) is $\left(\frac{\text{Joule}}{\text{second}}\right)$.

A 500-MW power plant produces 500-MJ of mechanical energy every second.

Efficiency is given as 40%. For the energy conversion in one second

$$\eta = \frac{W}{Q_h}$$

$$0.4 = \frac{500\text{MJ}}{Q_h}$$

$$Q_h = 1250 \text{ MJ}$$

The plant absorbs 1250 MJ of heat energy in one second from the fuel burning in the furnace.

500 MJ of this energy is converted into useful work.

The waste heat given out to the cold reservoir (the river) can be calculated by

$$Q_c = Q_h - W$$

$$Q_c = 1250 \text{ MJ} - 500 \text{ MJ}$$

$$Q_c = 750 \text{ MJ}$$

in one second.

The plant transfers heat energy to the river at a rate of 750 MW.

Example 5.12 Efficiency of an automobile engine

An automobile's motor develops 32 kW power while it travels 40 km at a constant speed of 80 km/h. During the journey it consumes 4 kg diesel fuel. Find the percent efficiency of the motor, if the heat of combustion of the fuel is 42 MJ/kg.

Solution

The journey takes

$$\text{time} = \frac{\text{distance}}{\text{speed}} = \frac{40\text{km}}{80\text{km/h}} = 0.5 \text{ h}$$

$$t = 1800 \text{ s}$$

Total useful energy developed by the engine along the journey is given by

$$W = Pt$$

The total heat energy produced by the combustion of fuel can be calculated by

$$Q = mq$$

where m is the mass of the fuel and q is the heat of combustion of the fuel.

The efficiency is

$$\eta = \frac{W}{Q_h} = \frac{Pt}{mq}$$

$$\eta = \frac{(32\times10^3\text{W})(1800\text{s})}{(4\text{kg})(42\times10^6\text{ J/kg})}$$

$$\eta = 0.34 \text{ or } 34\ \%.$$

5.10 THE SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics determines the direction of heat flow and restricts the usability of thermal energy for producing work.

The second law of thermodynamics can be phrased in different equivalent statements. Some of these are:

- It is impossible to completely convert thermal energy into work. In other words, no heat engine can have an efficiency of 100 percent (Figure 5.34).
- Heat cannot, by itself, flow from a colder body to a hotter body (Figure 5.35).

It has already been shown (section 5.8) that these two seemingly unrelated statements are equivalent. It is possible to express the second law in a third statement which is also equivalent to the first two:

- All naturally occurring processes increase disorder.

This third statement will be examined in further detail in section 5.13.

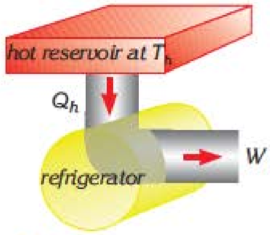


Figure 5.34 Impossible heat engine

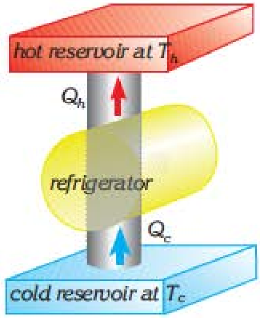


Figure 5.35 An impossible refrigerator

5.11 THE CARNOT ENGINE

The second law of thermodynamics does not allow us to construct a heat engine that is 100 percent efficient. What, then, is the maximum efficiency that can be attained by a heat engine? The question has great theoretical and practical importance.

A theoretical reversible cyclic process, called the 'Carnot cycle' has the maximum possible efficiency between two given heat reservoirs with definite temperatures.

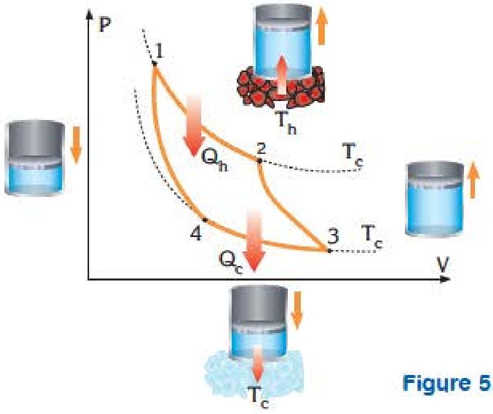


Figure 5.36 The carnot cycle

Remember, most heat engines work in cycles. The carnot cycle is the most efficient cycle allowed.

The Carnot Cycle consists of two adiabatic and two isothermal processes. All these processes are reversible. (Reversibility will be defined in the next section)

Referring to figure 5.36;

- Processes 2 - 3 and 4 - 1 are adiabatic. No heat is transferred.
- During process 1 - 2, gas expands isothermally, absorbing heat (Q_h) from a hot reservoir of temperature T_h.

- During process 3 - 4 gas is compressed isothermally, releasing heat (Q_c) to a hot reservoir of temperature T_h.

No engine, absorbing heat from a source at T_h and releasing heat to a reservoir at T_c, can be more efficient than a Carnot engine operating between the same temperatures.

Why then, aren't Carnot engines used in cars, if it is the most efficient engine?

This is because, it is a theoretical, reversible cycle which is impossible to construct in practice. A Carnot engine is useful to the extent that it allows a limit to the efficiency, between two given temperatures, to be calculated.

The efficiency of a real heat engine operating between given temperatures (T_h) and (T_c) is always lower than the efficiency of a Carnot engine operating between the same temperatures.

$$\eta_{real} < \eta_{Carnot}$$

This is because a real engine does not work on a Carnot cycle, and additional factors such as friction and heat losses decrease the efficiency.

The Efficiency of a Carnot Engine

The efficiency of a Carnot engine, absorbing heat from a hot reservoir at T_h and releasing heat to a cold reservoir at T_c is given by

$$\eta_{max} = 1 - \frac{T_c}{T_h}$$

The maximum possible efficiency of a heat engine is determined by the difference between T_h and T_c. A greater temperature difference results in a greater efficiency. Engines operating at higher temperatures and releasing exhaust gases at lower temperatures are more efficient.

Example 5.13 A Carnot heat engine

A Carnot heat engine receives heat from a high temperature heat source at 700 °C and releases heat to a low temperature heat sink (cold reservoir) at 27°C.

a) What is the efficiency of this engine?

b) What is the mechanical work output of the engine in one cycle, if it receives 400 kJ of heat from the hot reservoir in one cycle.

Solution

a) The first step to take is to express the given heat reservoir temperatures in Kelvins.

$T_h = 973$ K

$T_c = 300$ K

A Carnot engine operating between these two temperatures has an efficiency given by

$$\eta_{max} = 1 - \frac{T_c}{T_h}$$

$$\eta_{max} = 1 - \frac{300K}{973K}$$

$$\eta_{max} \approx 0.69$$

The efficiency of a Carnot engine between these temperatures is 69%.
The efficiency of a real engine absorbing heat from the same source and rejecting heat to the same sink, will be much lower than this value, as discussed above.

b) Using the definition of efficiency for a heat engine, useful work is given by

$$\eta = \frac{W}{Q_h}$$

$$W = \eta Q_h$$

$$W = (0.69) \times (400\ kJ)$$

$$W = 276\ kJ$$

400 kJ - 276 kJ = 124 kJ of energy heats the environment for each cycle.

5.12 THE NEED FOR A SECOND LAW. REVERSIBLE AND IRREVERSIBLE PROCESSES

Why do we need a second law of thermodynamics? This is because the first law alone is not sufficient to predict nature. Some physical processes never occur although, according to the first law, they are allowed. Consider the examples below:

- A hot object is placed in contact with a cold object. The first law of thermodynamics states that the amount of heat released by one of the objects equals the amount of heat absorbed by the other. It does not tell us the direction of heat flow. However, a hot object cannot get hotter by absorbing energy from a colder object. Heat always flow from a hot place to a cold place, as shown in Figure 5.37.
- Ice melts at room temperature, absorbing heat from the air. However, water never freezes by itself at room temperature, to release heat energy and make the room hotter.
- When a stone is dropped into water from a height, the water gets hotter. However a stone is never ejected back upwards into the air, making the water cooler again, as shown in Figure 5.38.
- A drop of ink allowed to fall into a glass of water is homogeneously distributed all over the available volume. However, it never gets concentrated at a point again.
- When 100 coins are placed carefully on a table all heads up and shaken, 100 heads will never come up again, even after 1 000 000 000 trials.

These events can never occur, since they violate the second law of thermodynamics.

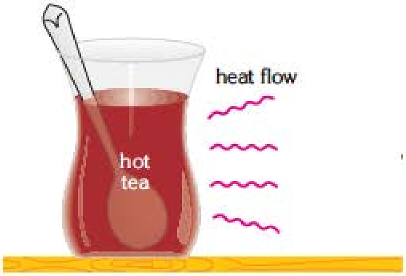


Figure 5.37 Hot tea doesn't get hotter by absorbing heat from cooler air.

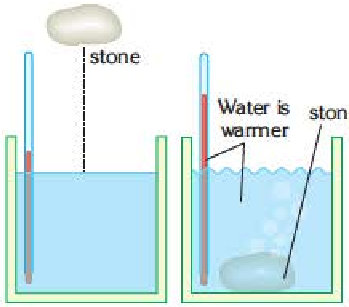


Figure 5.38 Water never ejects the stone upwards, so that the water, itself becomes cooler.

A **reversible process** can be reversed without leaving any trace of its occurrence on the surroundings. All processes that are not reversible are irreversible.

As the examples above show, all naturally occurring processes are irreversible. The effects of friction, mixing of two liquids or gases, heat transfer due to a temperature difference, chemical reactions, expansion of a gas in a vacuum… are irreversible.

The word irreversible does not mean that the system cannot be returned back to its initial state. As an example, a sliding block brought to a stop by friction can be given its initial velocity once again. However, the surroundings does work on the block to produce this velocity. Therefore a permanent change takes place in the surroundings. The block is returned to its initial state, but the environment is not. For this process 'sliding block, stopped by friction' to be reversible, the block must gain its initial velocity, absorbing back the energy turned into heat by friction. Naturally this is impossible. Nobody has ever witnessed an object getting colder and gaining a velocity.

Therefore a reversible process is actually an idealisation, which never really happens. Some processes are close to being reversible, however. Just like the ideal gas law indicates the behaviour of real gases, despite the fact that no gas is ideal; the reversible process model supplies us with useful information for understanding real processes.

Slow compression or expansion of a gas sample, in a frictionless cylinder-piston system, can be taken as reversible. Slow compression can be achieved by increasing the external pressure in infinitely small steps. Slow expansion requires the gas to be heated through infinitely small temperature differences. A fast process is irreversible, because the effects of the turbulence in the gas cannot be reversed.

5.13 ORDER AND DISORDER

What is the reason behind the irreversibility of all natural processes?

Physics laws do not normally answer 'why' questions. Laws of physics are formulated to answer 'how' questions. The universal law of gravitation describes how the gravitational force acts between two massive objects, but it does not explain why two masses attract each other.

Interestingly, the reason why all natural processes are irreversible can be explained. Once a few reasonable assumptions about molecules are accepted, it can be shown that all spontaneous processes are irreversible.

First **macrostates** and **microstates** of a system will be defined.

Suppose 4 coins are placed in a box, the box is shaken and the number of tails that have turned up after shaking are counted. This process is repeated many times and the number of tails is recorded each time.

The number of tails counted each time represents the macrostates of the system in this experiment.

Thus, the system has 5 macrostates: 0, 1, 2, 3 or 4 tails up. It may be guessed if we shake the box 10 000 times, we will end up with each macrostate approximately 2000 times.

However, when the experiment is repeated many times, some macrostates occur much more than others. After one million trials, the number of times 4 tails turned up is about 6 times lower than the number of times 2 tails turn up.

If the experiment is repeated with 100 coins, the box must be shaken 10^{30} (one thousand billion billion billion) times before all tails turn up. Nearly all the trials will result in the number of tails being around 50% (between 40% and 60%).

What is the reason behind this observation? Is there a physics law which prevents the coins from falling tails up all together? Do the coins push each other while falling the same side up?

The answer is that some macrostates are more probable than others, because they can happen in more ways. The number of ways in which a macrostate can occur are called the microstates of a system. For the 4 coins in the box, the macrostate '4 tails up' can occur only in one way, but the macrostate '2 tails up' can occur in 6 different ways. Table 5.1 demonstrates this fact:

Macrostates	Microstates						Number of microstates
0 tails	HHHH						1 microstate
1 tails	THHH	HTHH	HHTH	HHHT			4 microstates
2 tails	TTHH	THTH	THHT	HTTH	HTHT	HHTT	6 microstates
3 tails	HTTT	THTT	TTHT	TTTH			4 microstates
4 tails	TTTT						1 microstate

Table 5.1 Possible microstates for 4 coins.

As seen from the table, when 4 coins are tossed, there are ($2^4=16$) microstates in which 5 different macrostates can occur. However, the number of microstates is different for each macrostate. More ordered (organised) states are less likely to occur. For example the most ordered states are all the coins showing the same side up, but these states can occur only in one way. On the other hand, the most disordered state (2H, 2T) may occur in 6 different ways.

This is the reason why it is difficult to keep a bedroom tidy. There are many ways in which the room can be a mess. A shirt can be placed on the table, over the floor, under the sofa, etc... to make the room untidy, but there is only one proper place for the shirt; the wardrobe.

If 100 coins are tossed in place of 4, there are a total of ($2^{100} \approx 10^{30}$) possible microstates and only one of them is all tails (or heads) up. Therefore, practically, it will never happen.

Notice that, increasing the number of coins drastically increases the number of microstates. Consider a closed container, divided into two equal parts by a partition as in Figure 5.39. Initially, the left side is filled with an ideal gas, the right side is a vacuum. When the partition is removed, the gas expands until the numbers of molecules on both sides are nearly equal. It was assumed that it was an ideal gas, so the gas molecules do not pull or push each other. Why then, does the gas divide itself equally between the two parts? Why does the reverse process (all the gas accumulating on the left again) never occur by itself?

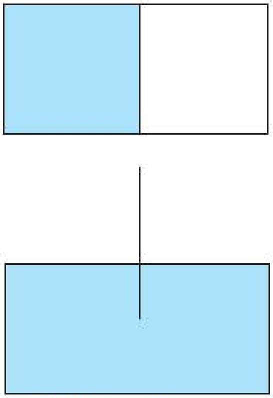


Figure 5.39 The gas is equally distributed between the two sections when the partition is removed

This is because each gas molecule may be on the left or right side of the box, with equal probability. This is analogous to a coin coming up tails or heads with equal probability.

Now suppose that the gas consists of 10^{23} molecules. Since there are 2 cases for each molecule, the total number of ways in which the molecules can be distributed is $2^{(10^{23})}$. However, for the most ordered case, all molecules must be on the same side, and this can happen only in one way. It is possible, but not probable. It will never happen.

We saw that all naturally occurring events are irreversible. This is because all naturally occurring events go from order to disorder.

One of the examples given in section 12, was the stone falling in water, as shown in Figure 5.38. The water molecules become faster, on average, after the stone has fallen, however, they never eject the stone back into the air. For this to happen, at a given instant, all the water molecules must move in the same direction in an ordered manner, all pushing the stone upwards together.

This is possible (there is no physics law to prevent it), but not probable.

While the stone is falling, all molecules in the stone move in the same direction. The stone can do useful work, it can push an object.

Once it hits the water, the 'ordered' energy of the stone is transferred to the water molecules moving in a 'disordered' manner. The amount of energy has not changed, but the energy has now spread out over many molecules, moving in a random way. Water molecules will never use this energy, re-ordering it to all, to come together and act in an ordered way. Energy is not lost, but it is not useful anymore.

The second law of thermodynamics can now be re-phrased in terms of order and disorder.

Isolated systems tend towards disorder

Therefore in a sufficiently long time, all the energy in the universe will become useless, although the total amount of energy will not have changed. There will be no useful energy to do work and all substances will be equally hot (or cold). This is called the heat death of the universe.

Contrary to many physics laws, the statements of the second law discussed, are qualitatitive. To be able to write a quantitative formula for the second law, a quantity called 'entropy' is defined. Entropy is the quantitative measure of disorder. Using entropy, the second law can be re-stated as follows:

Entropy of an isolated system either increases or at best stays constant during any change.

It is possible to show that heat flowing from a cold body to a hot body by itself will decrease in total entropy. The second law of thermodynamics requires heat to flow from a hot body to a cold body; increasing the entropy (and disorder). Therefore all statements of the second law are equivalent.

Question

Why are we trying to save energy if total energy never changes?

Answer

What we are trying to save is not energy, but useful energy that can do work.

But why is the useful energy decreasing? Can't it be re-gained, if it is not lost? The answer is no, unfortunately. Heat is released during all energy transformations, due to friction and other effects. Consider the examples below:

- Charging a battery converts electrical energy into chemical energy but the battery heats up.
- A car motor converts chemical energy, hidden in the gasoline, into mechanical energy, but the motor and the exhaust gas heat the surroundings.
- A generator converts mechanical energy into electrical energy, but the wires heat up when current flows.

The second law of thermodynamics shows that, once one type of energy turns into thermal energy, it cannot be re-gained completely. Since thermal energy is produced during all energy transformations, all the useful energy in the universe will ultimately turn into useless energy of the random motion of molecules. At the end, the total amount of energy will not have changed, but all energy transformations will have stopped.

The usability of energy is hidden in the orderly motion of molecules. A flying bullet has kinetic energy which can push a piston, because all the molecules in the bullet are moving in the same direction. This orderly energy is useful because it can do work.

On the other hand, if a piston (from the gas-piston system) has hot steam on both sides, the sum of the energies of the molecules, on both sides, is higher than the kinetic energy of the bullet, and the amount of energy is more than enough to push the piston. However, molecules on one side do not suddenly start to move in the same direction and push the piston. If, molecules on one side were slower on average, they would apply a lower pressure on average, so the piston would move, turning part of the thermal energy into mechanical energy. Therefore, the parameter that turns thermal energy into mechanical energy is not high temperature, but temperature difference.

The fate of all useful energy in the universe is the same: being converted into thermal energy. In the gas piston example, pushing the piston decreases the temperature difference, (hot side cools, cool side gets hotter) and the mechanical energy gained by the piston will ultimately turn into thermal energy.

Summary

Definitions

$$\text{Efficiency} \equiv \frac{\text{Useful output}}{\text{Total input}}$$

An **adiabatic process** is a process during which a system does not exchange heat with the surroundings.

An **isothermal process** is a process which occurs at constant temperature.

An **isovolumetric process** is a process which occurs at constant volume.

Laws and Principles

First law of thermodynamics

$$Q = \Delta U + W_{\text{by system}}$$

Second law of thermodynamics, (three equivalent statements)

- It is impossible to convert thermal energy completely into work. In other words, no heat engine can have an efficiency of 100 percent.
- Heat cannot, by itself, pass from a colder body to a hotter body.
- Isolated systems tend towards disorder.

The Carnot engine has the maximum possible efficiency between two given heat reservoirs with definite temperatures.

Efficiency of a Carnot engine:

$$\eta_{\text{max}} = 1 - \frac{T_c}{T_h}$$

Pressure, volume, temperature and internal energy are state variables.

Heat and work are path dependent.

Other Formulas

Work in a thermodynamic process

$$W = P\Delta V = nR\Delta T \qquad (P = \text{const})$$

Efficiency of a heat engine

$$\eta = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

QUESTIONS AND PROBLEMS

(Take 1 atm=100 kPa, g=10 N/kg)

5.1 Definitions

1. Define the following terms:

- System and surroundings
- State of a gas
- State variable
- Equilibrium state
- Thermal process

5.2 Internal Energy of a Gas

2. What is the difference between the internal energy of a gas sample and the internal energy of a solid object?

3. Why can't we change the internal energy of a gas sample without changing its temperature?

4. On which macroscopic parameters does the internal energy of an ideal gas depend?

5.3 Transferring Energy to a System

5. Both heat and work are means of transferring energy to a system. What is the difference between them?

6. Does the energy of a system increase or decrease, when it does work on the surroundings?

7. Does the energy of a system increase or decrease when the surroundings do work on the system?

8. What is the relationship between work done by a system and work done on a system?

9. Does a gas sample do positive or negative work as its volume increases against external forces?

5.4 The First Law of Thermodynamics

10. What happens to heat given to a system according to the first law of thermodynamics?

11. A gas sample does 320 J of work, as it absorbs 700 J heat from the surroundings. What is the internal energy change of the gas?

12. The internal energy of a gas sample increases by 280 J when it does 185 J of work. What amount of heat is absorbed by the gas?

13. 800 J of work is done on a gas sample as it releases 150 J of heat. What is the internal energy change of the gas?

14. The internal energy of a system increases by 100 J, when it absorbs 400 cal heat. What is the work done by the system on the surroundings?

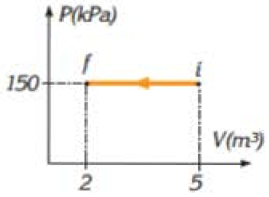
15. A gas in a closed container absorbs 450 J heat. What is the internal energy change of the gas?

5.5 Work in a Thermodynamic Process

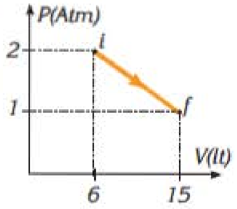
16. A gas sample slowly expands from 2 lt to 5 lt against constant standard atmospheric pressure. What is the work done by the gas?

17. A gas expands slowly against a constant pressure of 200 kPa, doing 100 J work during the expansion. What is the volume change of the gas?

18. A gas sample in a cylinder-piston system is slowly compressed from state (i) to state (f) as, in the P-V graph shown in the figure. What is the work done by the gas during compression?



19. A gas expands as shown in the P-V graph. What is the work done by the gas during expansion?



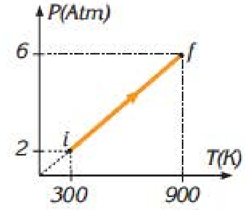
20. 12 g of helium gas is heated from 20 °C to 200 °C, at a constant pressure. What is the work done by the helium gas during the heating process? ($M_{He}=4$ g/mole)

21. An ideal gas expands isobarically at 100 kPa. The volume of the gas increases by 0.5 lt as it absorbs 175 J heat. What is the internal energy change of the gas?

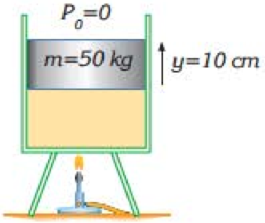
22. Internal energy of a gas increases by 150 J as it absorbs 250 J heat under 100 kPa of constant pressure. What is the change in volume in cm^3?

23. The temperature of 56 g of nitrogen gas increases from 20 °C to 200 °C, as it absorbs heat at constant pressure. The internal energy of the gas increases by 7 480 J during the process. What is the amount of heat absorbed by the gas? (Take $M_{N_2}=28$ g/mole)

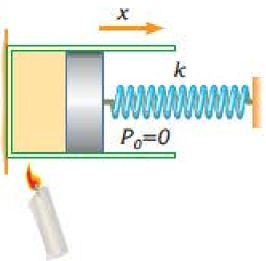
24. The figure shows a P-T graph for an ideal gas. What is the internal energy change of the gas between states (i) and (f), if it absorbs 1 800 J heat during the process?



25. The gas sample in the frictionless cylinder-piston system in the figure expands against the weight of the piston, as it absorbs 175 J heat energy. The mass of the piston is 50 kg. What is the internal energy change of the gas during the process? Take atmospheric pressure to be zero.



26. The gas sample, in the figure aside, compresses the spring connected to the piston by x=10 cm, as it absorbs heat from outside. During the process, internal energy of the gas increases by 100 J. The spring is initially uncompressed. What amount of heat energy is absorbed by the gas during the process? Take atmospheric pressure as zero, the spring constant as k=8 000 N/m.

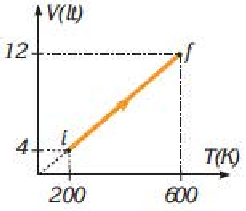


27. The work done by a gas is equal to one quarter of the increase in its internal energy, as it absorbs 480 J of heat. What is the change in the internal energy of the gas?

28. The temperature of 2 moles of an ideal gas increases from 20 °C to 120 °C, as it absorbs 5 817 J of heat at constant pressure. What is the change in the internal energy of the gas?

29. A gas sample, initially having a volume of 2 lt, slowly expands against a constant 100 kPa pressure. During the expansion the gas absorbs 2 100 J of heat and its temperature increases from 300 K to 1 200 K. What is the internal energy change of the gas?

30. 2 moles of an ideal gas expands from (i) to (f), as shown in the figure above. What is the change in the internal energy of the gas, if 16 620 J heat flows into the gas during the expansion.

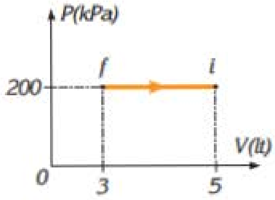


31. 250 J of heat is transferred to a gas sample in a cylinder-piston system initially at 27 °C. The movable piston keeps the pressure constant at 1 atm. The initial volume of the gas is 3 lt. What is the change in the internal energy of the gas, if the final temperature becomes 127 °C?

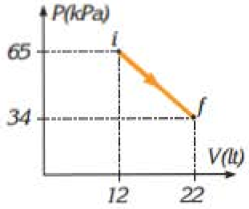
32. One mole of water, at 100 °C, completely boils away under standard atmospheric pressure. What is the change in the internal energy of the water? 1 mole of water vapour occupies a volume of 0.03 m^3 at 100 °C, under 1 atm pressure. (Take L_V=2 260 kJ/kg M_{water}=18 g/mole)

5.6 State Variables and Path Dependent Variables

33. The P-V graph for 0.2 moles of an ideal gas is given in the figure. Determine the initial and final temperatures of the gas.



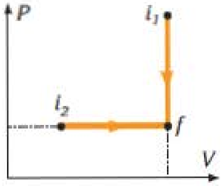
34. One mole of an ideal gas expands from (i) to (f) along the line shown in the figure.



a) Has the gas become hotter or colder at the end of the process?

b) What is the work done by the gas.

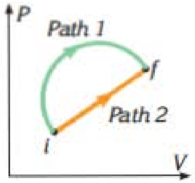
35. The initial states of two ideal gas samples, containing the same number of moles, are represented by i_1 and i_2 in the P-V graph in the figure. The gases are then brought to the same final state 'f' along two different processes.



a) Which gas is hotter at the end?

b) Which gas has more internal energy at the end?

36. An ideal gas sample expands from state 'i' to state 'f' along two different paths, as shown in the P-V graph above. Compare:



a) The net works done by the gas

b) The internal energy changes of the gas

c) The net heats absorbed by the gas along the two different paths.

5.7 Thermal Processes

37. Define an adiabatic process. How can we achieve an adiabatic process?

38. One mole of a gas sample is compressed to half of its original volume. Is the gas hotter at the end of an adiabatic or isothermal compression?

39. A gas sample expands from initial volume V_1 to final volume V_2 once isobarically and once along an isotherm. Along which process does the gas do more work?

40. In which process (isobaric or isothermal) between two given states does a gas absorb more heat?

41. What happens to the heat absorbed by a gas during an isothermal process?

42. The volume of a gas in a cylinder-piston system is decreased to half its initial value, as a result of a sudden compression. Does the pressure increase to twice its original value?

43. One mole of an ideal gas is adiabatically compressed from 3 lt to 2 lt. During the compression 300 J of work is done on the gas. What is the change in the internal energy of the gas?

44. One mole of an ideal gas expands adiabatically, doing 20 J work on the surroundings during the expansion. What is the change in the internal energy of the gas, if the initial volume is 0.015 m^3?

45. An ideal gas sample isothermally expands from 0.3 lt to 0.8 lt. What is the change in the internal energy of the gas during the process, if its initial temperature is 300 K?

46. One mole of an ideal gas is compressed to one quarter of its original volume, isothermally. The initial volume of the gas is 0.005 m^3. During the compression 112 J of work is done on the gas.

a) What is the change in the internal energy of the gas?

b) How much heat does the gas exchange with the surroundings?

47. A gas sample absorbs 200 J of heat at constant volume. What is the change in the internal energy of the gas?

48. The temperature of 500 g of aluminum increases from 20 °C to 200 °C. What is the change in the internal energy of the aluminum? Assume the volume remains constant. (Take c_{Al}=900 J/kg.C)

49. A 1-kg lead block cools from 20°C to -30°C. What is the change in the internal energy of the block? (Take c_{Pb}=128 J/kg.C)

50. What is the change in the internal energy of 200 g of ice, as it melts at 0 °C. Neglect any volume change. (Take L_f=335 000 J/kg)

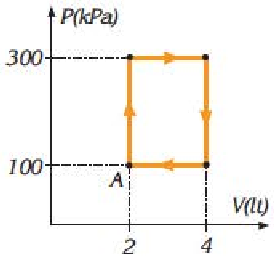
51. Why does the specific heat for most substances increase with increasing external pressure? (The values listed in table 4.1 are measured under 1 atm pressure)

52. The specific heat of iron under 1 atm pressure is 460 J/kg °C. The temperature of an m=7.9-kg, (V=0.001-m^3 iron) block increases by ΔT= 100 °C, under 1 atm pressure. What is the change in the internal energy of the block:

a) If the small change in volume is neglected

b) If the thermal expansion is taken into consideration (Take $\alpha_{iron}=10^{-5}$ 1/°C)

53. An ideal gas undergoes a cyclic process as shown in the P-V graph.

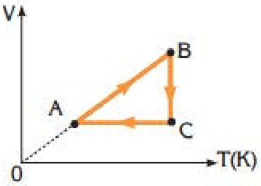


a) What is the net heat absorbed by the gas in one complete cycle

b) Find the temperature of the gas at the corners, if T_A=300 K?

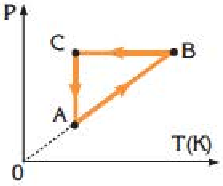
54. A gas sample confined to a cylinder by a movable piston undergoes the process described in the V-T graph shown.

Transfer the same process to a P-V graph.

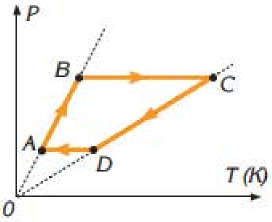


55. A gas sample confined to a cylinder, by a movable piston, undergoes the process described in the P-T graph.

Draw the corresponding P-V and V-T graphs for the same process.



56. An ideal gas traces the curve shown in the figure. Transfer the process to P-V and V-T graphs.



5.8 Heat Engines

57. What is a heat engine?

58. A heat engine produces 3 000 J of heat during the combustion of fuel and releases 2 000 J of heat from its exhaust. What is the efficiency of this engine?

59. A heat engine of η=0.3, loses 5 000 J heat during one cycle. What is the work done by the engine in one cycle?

60. A steam power plant burns 50 tons of coal every hour. The useful power output of the plant is 130 MW (megawatts =10^6 watts). What is the efficiency of this plant? (Take q_{coal}= 30 MJ/kg)

61. A 500 MW (megawatt) steam power plant has an efficiency of 0.45.

a) What is the useful energy produced by the plant per day?

b) How much heat energy is released to the surroundings per day?

62. An automobile's motor develops 32 kW power while it travels 40 km at a constant speed of 80 km/h. During the journey it consumes 4 kg of diesel fuel. Find the percent efficiency of the motor if the heat of combustion for the fuel is 42 MJ/kg

63. How much diesel fuel does an automobile consume in 300 km, if it travels at a constant speed of 75 km/h? The car's engine develops 70 hp (≈52 kW) of useful power during the journey. The efficiency of the car's engine is 0.3. (Take q_{diesel}= 42 MJ/kg)

5.9 Refrigerators and Air Conditioners

64. Does a refrigerator heat or cool the kitchen, if it operates with its door open?

65. The motor of an air conditioner does 3000 J of work, as it pumps out 2000 J of heat from the cooler interior of a house to the warmer street. What is the total heat released to the street air?

5.10 The Second Law of Thermodynamics

66. What are the three different statements of the second law of thermodynamics?

5.11 The Carnot Engine

67. Could a heat engine have a 100% efficiency, if friction, heat losses to the surroundings, etc. were eliminated?

68. a) What maximum efficiency can a steam engine have if it absorbs hot steam at 800 °C and exhausts it at 120 °C?

b) Explain why this engine can never reach this theoretical efficiency value?

69. What is the efficiency of a Carnot engine which operates between the temperatures T_h=1 200 K and T_c= 300 K?

70. A Carnot engine operates between a hot reservoir at 327 °C and a cold reservoir at 27°C. How much work does the engine do if it absorbs 800 J heat from the hot reservoir?

71. An ideal heat engine produces 400 J of mechanical work for each 900 J of energy it absorbs from the hot reservoir. What is the absolute temperature of the hot reservoir, if the temperature of the cold reservoir is 350K?

5.12 The Need for a Second Law. Reversible and Irreversible Processes

72. Define reversible and irreversible processes.

73. Why can't a heat engine use the immense internal energy stored in ocean water?

74. Classify the following events into two groups:

A. Allowed by first law, hindered by second law

B. Hindered by both first and second laws

a) A heat engine absorbs 100 J of heat and does 100 J work

b) A heat engine absorbs 100 J of heat and does 110 J of work

c) During a heat exchange between an isolated two-body system, the cold body releases 20 J of heat, the hot body absorbs 20 J of heat.

d) A coin lying on a table suddenly gets colder by itself and is ejected upwards.

e) A glass of water at room temperature turns into ice, making the air slightly hotter.

f) A mixture of salt and pepper is separated by shaking.

5.13 Order and Disorder

75. What is the physical parameter used for numerically measuring the degree of disorder?

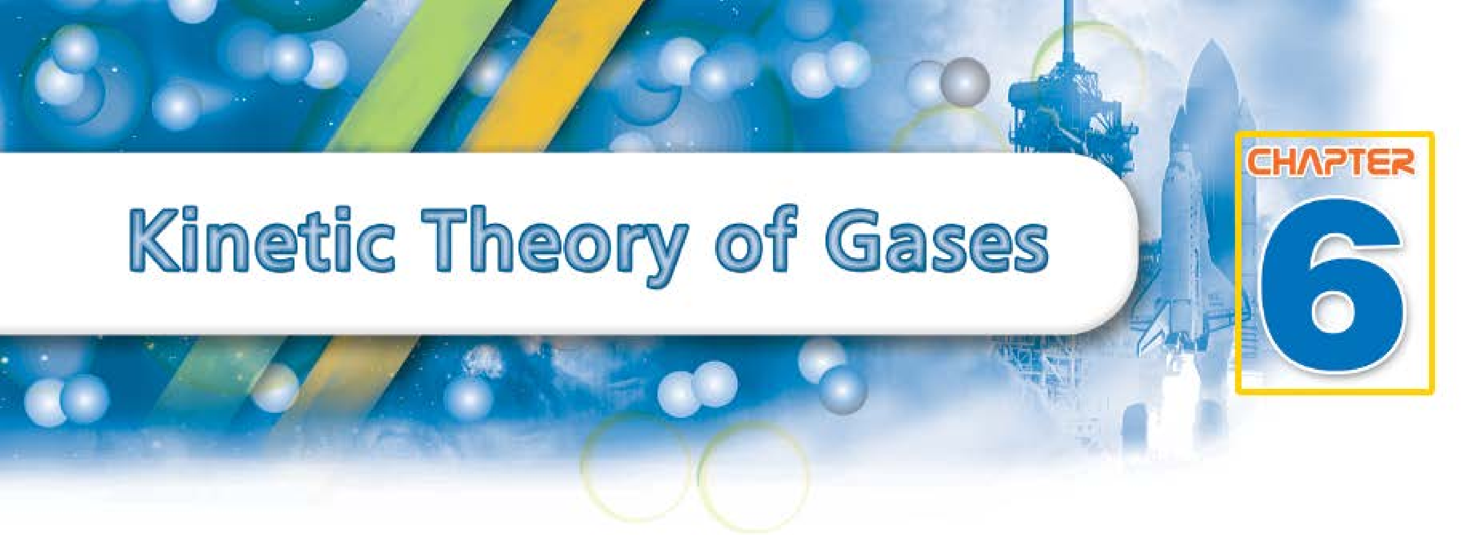
76. Four coins are tossed 1 000 000 times.

a) How many times should we expect to see 4 tails come up?

b) How many times should we expect to see 2 tails and 2 heads come up?

c) Why does the event '2 tails up' occur much more frequently than '4 tails up'? Does a coin know what others are doing?

77. Why is everybody trying to save energy, if energy is already a conserved quantity?



CHAPTER 6

Kinetic Theory of Gases

Kinetic theory applies the laws of mechanics to the motion of molecules, using simple averaging techniques.

Thermodynamics describes macroscopic quantities, such as pressure, temperature, and volume. The laws of thermodynamics do not make any reference to the molecular structure of matter. In fact the laws of thermodynamics were settled while the existence of atoms was still speculation.

The gas laws and the laws of thermodynamics can be explained, by assuming that matter is made up of small particles, in continuous random motion, as in chapters 3, 4 and 5. However, the explanations were qualitative in the preceding chapters. In this chapter a quantitative analysis of the relationship between the motion of molecules and macroscopic properties such as pressure or internal energy of a gas will be discussed, using the methods of the kinetic theory.

Kinetic theory applies the laws of mechanics to the motion of molecules, using simple averaging techniques.

The past chapters have emphasised that 'temperature is a measure of the average kinetic energy of molecules'. Starting from simple assumptions and applying Newton's laws to molecules, the quantitative relationship between the temperature of a gas and the average kinetic energy of molecules will be determined.

6.1 ROOT MEAN SQUARE VALUE

The root mean square (rms) value of a variable has a similar meaning to the average value. Comparing average speed (v_{av}) and root-mean-square speed (v_{rms}) of three particles of speeds 10 m/s, 20 m/s and 30 m/s, will provide an understanding of the meaning of the rms value of a quantity. Figure 6.1 shows the particles confined in a box.

Average value is defined as:

$$v_{av} = \frac{v_1 + v_2 + v_3}{3}$$

The average value of speed is thus

$$v_{av} = \frac{(10\ \text{m/s}) + (20\ \text{m/s}) + (30\ \text{m/s})}{3} = 20\ \text{m/s}$$

The root mean square speed is the square root of the mean (=average) of the squares of the velocities:

$$v_{rms} \equiv \sqrt{\frac{v_1^2+v_2^2+v_3^2+\ldots+v_N^2}{N}}$$

v_{rms} of three particles is

$$v_{rms} = \sqrt{\frac{(10\ m/s)^2+(20\ m/s)^2+(30\ m/s)^2}{3}} = 21.6\ m/s$$

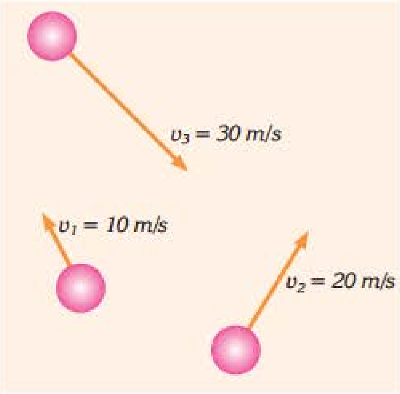


Figure 6.1 Three particles in a box

The average value of a quantity is represented by a bar over the symbol. For example for average speed one of the two symbols: $v_{av} \equiv \overline{v}$ can be used.

$\overline{v^2}$ means the average value of the squares of the speeds. In the example above,

$$\overline{v^2} = \frac{v_1^2+v_2^2+v_3^2}{3} \approx 467\ m^2/s^2.$$

Therefore

$$\overline{v^2} = v^2_{rms}$$

since $\sqrt{\overline{v^2}} = v_{rms}$ by definition.

On the other hand, $\overline{v}^2$ means the square of the average speed. In the example above

$$\overline{v}^2 = (\overline{v})^2 = \left(\frac{v_1+v_2+v_3}{3}\right)^2 = 400\ m^2/s^2.$$

Three Dimensional Velocity

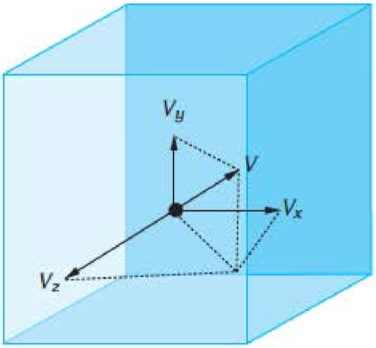


Figure 6.2 Three dimensional velocity

The velocity of a gas molecule has three components: v_x, v_y, v_z, as shown in Figure 6.2. Pythagorean Theorem can be used to relate the magnitudes: $v^2=v_x^2+v_y^2+v_z^2$.

Since the particle can move in all directions, with equal probability, the average values of the velocity components can be taken to be equal; $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$. Thus

$v^2 = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\,\overline{v_x^2} = 3\,\overline{v_y^2} = 3\,\overline{v_z^2}$.

Or

$$\overline{v_x^2} = \frac{\overline{v^2}}{3}.$$

6.2 THE PRESSURE OF AN IDEAL GAS

The pressure of a gas is caused by the motion of its molecules. If gas molecules cease moving, the gas pressure drops to zero. The relationship between the motion of gas molecules and gas pressure will now be derived. Before starting, the assumptions of kinetic theory about ideal gases will be reviewed:

- All matter is made up of molecules endlessly moving around in a random fashion.

- Gas molecules obey Newton's laws of motion.
- The total volume of gas molecules is nearly zero, compared to the total volume of the gas. This means that if the gas molecules stop moving, the volume becomes zero.
- There is no force between gas molecules, except during a collision.
- Collisions between gas molecules, or between the walls of a container and gas molecules are elastic. This means the total kinetic energy does not change.

The statements above are assumptions, which are simplifications of real cases, to make calculations simpler. No real gas acts totally in accordance with these assumptions. Nevertheless, experiments show that the formulas derived using these assumptions give reasonably correct results.

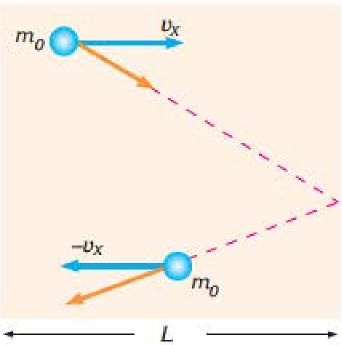


Figure 6.3 The change in velocity during a collision

The relationship between the pressure of an ideal gas and the average kinetic energy of molecules is given by

$$P=\frac{2}{3}n_u\left(\frac{1}{2}m_0\overline{v^2}\right)$$

This equation is called the 'fundamental equation of the kinetic theory', where, n_u is the molecular concentration,

This equation will now be derived, using the assumptions of the kinetic theory.

Consider a gas molecule in a cubic container of side length L. The mass of the molecule is m_0, the x component of velocity is parallel to one side of the cube. The force applied by the side wall upon a molecule is along the x axis.

$$F_x = m_0a_x$$

$$F_x = m_0\frac{\Delta v_x}{\Delta t}$$

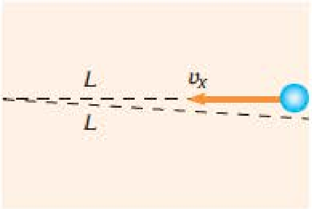


Figure 6.4 The time between two collisions equals the the total distance travelled between collisions, divided by the speed of the molecule

The change in the x component of velocity is given by $\Delta v_x = (-v_x) - (v_x) = -2v_x$, as shown in Figure 6.3. The time between collisions equals $\Delta t=\frac{2L}{v_x}$ (Figure 6.4). The average force on the molecule is

$$F_x=-m_0\frac{2v_x}{2L/v_x}$$

The force applied by the molecule upon the wall is opposite to the force applied on the molecule by the wall. This is shown in as shown in Figure 6.5.

$$F_x=m_0\frac{v_x^2}{L}$$

The total force applied upon the wall by N molecules is

$$F_x=Nm_0\frac{\overline{v_x^2}}{L}$$

since $v_1^2+v_2^2+...+v_N^2=N\overline{v^2}$. Now v_x^2 can be replaced by $\frac{\overline{v^2}}{3}$

$$F_x=m_0\frac{\overline{v^2}}{3L}$$

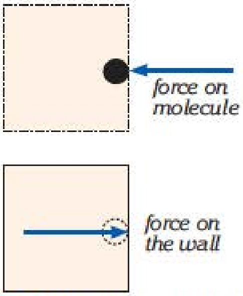


Figure 6.5 An action - reaction pair

This is the total force on the right wall. To find the pressure, divide by the area, A, of the wall, $A = L^2$, thus

$$P = Nm_0 \frac{\overline{v^2}}{3L^3}$$

However, L^3 is the volume of the cubic container. Denoting volume by V,

$$P = \frac{1}{3}\left(\frac{N}{V}\right)m_0\overline{v^2} \quad \text{or} \quad P = \frac{1}{3}n_u m_0 \overline{v^2}$$

The same expression can be written in terms of the average kinetic energy of a single molecule. Dividing and multiplying by 2 gives

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m_0\overline{v^2}\right)$$

Therefore, the pressure of a gas is proportional to:

a) Molecular concentration (n_u)

b) The average kinetic energy of the gas molecules.

Both factors increase the momentum delivered to the wall by the gas molecules in unit time.

Increasing n_u increases the number of impacts on the wall in unit time. Increasing the average kinetic energy, increases both the momentum transfer during one collision and the number of collisions in unit time.

Exercise 6.1 Gas pressure from molecular speed

What is the absolute pressure exerted by oxygen gas, in a closed container, having 4.5×10^{25} molecules/m^3 concentration, if the root-mean-square speed of the gas molecules is 500 m/s? (Take M_{O_2}=32 g/mole)

Solution

First find the mass of one oxygen molecule

$$m_0 = \frac{M}{N_A} = \frac{0.032 \text{ kg/mole}}{6\times10^{23} \text{ molecules/mole}}$$

$m_0 \approx 5.3\times10^{-26}$ kg/molecule for O_2 molecules.

To find the pressure

$$P = \frac{2}{3}n_u\left(\frac{1}{2}m_0\overline{v^2}\right)$$

In place of $\overline{v^2}$, v^2_{rms} can be used, as described above.

$$P = \frac{2}{3}n_u\left(\frac{1}{2}m_0 v^2_{rms}\right)$$

$$P = \frac{2}{3} \times \left(4.5 \times 10^{25} \times \frac{1}{m^3}\right) \times \left(\frac{1}{2}\left(5.3 \times 10^{-26}\ \text{kg}\right)\left(500^2\ \frac{m^2}{s^2}\right)\right)$$

$$P \approx 2 \times 10^5 \text{Pa}$$

$$P \approx 2\ \text{atm}$$

Exercise 6.2

Density from molecular speed

What is the density of nitrogen gas under 100 kPa pressure, if the root mean square velocity of nitrogen molecules is 480 m/s?

Solution

Using the fundamental equation

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2} m_0 \overline{v^2}\right)$$

$$P = \frac{1}{3} \frac{N m_0\ \overline{v^2}}{V}$$

However, $N \cdot m_0$ is the total mass of the gas. Thus, the equation is re-written as

$$P = \frac{1}{3} \frac{(N m_0)\overline{v^2}}{V}$$

$$P = \frac{1}{3}\left(\frac{m}{V}\right)\overline{v^2}$$

$$P = \frac{1}{3} \rho \overline{v^2}$$

$$P = \frac{1}{3} \rho v_{rms}^2$$

Substituting the numeric values,

$$\rho = \frac{3P}{v_{rms}^2} = \frac{3 \times 10^5 \text{Pa}}{480^2\, m^2/s^2}$$

$$\rho = 1.3\ \text{kg}/m^3$$

6.3 THE RELATIONSHIP BETWEEN TEMPERATURE AND MOLECULAR KE

Until now, the fact that the temperature of a gas is a measure of the average kinetic energy of gas molecules has been repeated many times. This statement will now be proved.

Currently there are two formulas for gas pressure:

- The ideal gas law is an empirical law. It is derived from experiment. The ideal gas law written in terms of molecular concentration is:

$$P = n_u kT$$

- The fundamental equation of kinetic theory. As seen above, this equation can be derived by applying Newton's laws to the gas molecules.

$$P = \frac{2}{3} n_u \left(\frac{1}{2} m_0 \overline{v^2} \right)$$

The pressure expressions in both equations are equal, so

$$\frac{2}{3} n_u \left(\frac{1}{2} m_0 \overline{v^2} \right) = n_u kT$$

Rearranging

$$\left(\frac{1}{2} m_0 \overline{v^2} \right) = \frac{3}{2} kT$$

Since 3/2 and k are constants, the equality indicates that:

'**Average kinetic energy** $\left(\frac{1}{2} m_0 \overline{v^2} \right)$ **of gas molecules depends only on temperature**'.

The equation can be re-written as

$$T = \frac{2}{3k} \left(\frac{1}{2} m_0 \overline{v^2} \right)$$

'Temperature of a gas is a direct measure of the average kinetic energy of gas molecules'.

6.4 ROOT-MEAN-SQUARE VELOCITY

The root-mean-square velocity, v_{rms} of the molecules of an ideal gas depend on two factors:

- Temperature
- Molecular mass

To formulate the relationship, the average molecular kinetic energy - temperature relationship is used.

$$\left(\frac{1}{2} m_0 \overline{v^2} \right) = \frac{3}{2} kT$$

$$\overline{v^2} = \frac{3kT}{m_0}$$

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m_0}}$$

$$v_{rms} = \sqrt{\frac{3kT}{m_0}}$$

The last equation can be written in terms of molar mass (M), rather than molecular mass (m_0), as it will be difficult to handle molecular mass in problems.

Using the equality $m_0 = \frac{M}{N_A}$ in the last equation

$$v_{rms} = \sqrt{\frac{3kT}{M/N_A}} = \sqrt{\frac{3(kN_A)T}{M}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Where the identity $k = \frac{R}{N_A}$ was used in the last step.

Exercise 6.3 Molecular speed from temperature

Find the root-mean square velocity of oxygen molecules at room temperature, $T \approx 20$ °C. (Take M_{O_2}=32 g/mole)

Solution

Treating oxygen as an ideal gas, the v_{rms} formula just derived can be used

Take care not to use the gram or centigrade units in the formula.

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$v_{rms} = \sqrt{\frac{3\times(8.31\ \mathrm{J/K})\times(293\ \mathrm{K})}{(0.032\ \mathrm{kg})}}$$

$$v_{rms} = 478\ \mathrm{m/s} = 1720\ \mathrm{km/h!}$$

So the oxygen molecules in the air around us are moving (on average) faster then jet planes, undergoing about 1 000 000 000 intermolecular collisions each second.

Exercise 6.4 Comparing average kinetic energies

A closed vessel contains an oxygen and helium mixture at 120 °C, under 2 atm of pressure. Which gas molecules have a greater translational kinetic energy on average? (Take M_{O_2} = 32 g/mole, M_{He}= 4 g/mole)

Solution

Translational kinetic energy is expressed as $\frac{1}{2}mv^2$.

Actually neither the molar mass nor the pressure are required to solve this problem. The average kinetic energy of gas molecules depends only on temperature. Since the two gases have equal temperatures, the average translational kinetic energies of gas molecules will also be equal.

$$T_{O_2} = T_{He}$$

$$\frac{1}{2}m_{O_2}\overline{v_{O_2}^2} = \frac{1}{2}m_{He}\overline{v_{He}^2} = \frac{3}{2}kT = 8.1\times10^{-21}\mathrm{J}$$

However, the molecular (rms) speeds of two gases are not equal. Since oxygen molecules are heavier, they will be moving more slowly than helium molecules at the same temperature.

Exercise 6.5

Heavier means slower

Determine the ratio of the rms speeds of oxygen and hydrogen molecules at the same temperature. (Take M_{O_2} =32 g/mole, M_{H_2} =2 g/mole)

Solution

For two gases at the same temperature,

$$T_1 = T_2$$

$$\frac{3}{2}kT_1 = \frac{3}{2}kT_2$$

$$\frac{1}{2}m_1\overline{v_1^2} = \frac{1}{2}m_2\overline{v_2^2}$$

$$\frac{\overline{v_1^2}}{\overline{v_2^2}} = \frac{m_2}{m_1}$$

$$\sqrt{\frac{\overline{v_1^2}}{\overline{v_2^2}}} = \sqrt{\frac{m_2}{m_1}}$$

$$\frac{v_{rms1}}{v_{rms2}} = \sqrt{\frac{m_2}{m_1}}$$

The ratio of molar masses can be used in place of the ratio of molecular masses, as described

$$\frac{v_{rms_1}}{v_{rms_2}} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}}$$

The root-mean-square speed ratio of two gases, at the same temperature, is inversely proportional to the ratio of the square root of the molar masses.

For hydrogen and oxygen

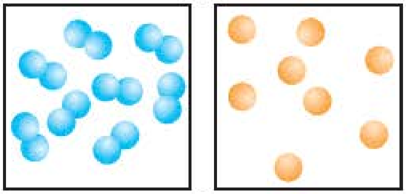
$$\frac{v_{H_2}}{v_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} = \sqrt{\frac{32\text{ g}}{2\text{ g}}} = 4$$

So the hydrogen molecules move 4 times faster on average.

6.5 INTERNAL ENERGY OF GASES

Helium (He), neon (Ne), argon (Ar), radon (Rn), etc. are monatomic gases, since molecules of these gases consist of single atoms.

Hydrogen (H_2), nitrogen (N_2), oxygen (O_2), etc. on the other hand, are called diatomic, because their molecules consist of two atoms, as shown in Figure 6.6.



8 molecules of nitrogen gas

8 molecules of helium gas

Figure 6.6 Monatomic and diatomic molecules

Molecules having more than two atoms are called 'polyatomic molecules' in general.

As stated earlier, the molecules are assumed to be of an ideal gas, that do not exert a force upon each other as long as they don't collide. Thus, the intermolecular potential energy of ideal gas molecules is zero. The only contribution to the total internal energy of a gas sample is from the kinetic energies of the molecules.

There may be many types of kinetic energy.

A diatomic gas molecule can possess three types of kinetic energy:

- Translational kinetic energy: Energy due to the motion of the molecule as a whole. $KE_{\text{translational}} = \frac{1}{2}m_0v^2$, where m_0 is the total mass of the molecule, as shown in Figure 6.7 a.
- Rotational kinetic energy: Energy of a molecule due to rotation about the centre of mass, as shown in Figure 6.7 b.
- Vibrational kinetic energy: Kinetic energy of oscillations about the centre of mass, as shown in Figure 6.7 c.

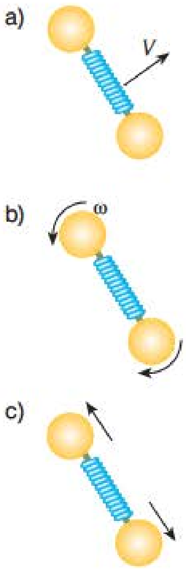


Figure 6.7 Three types of kinetic energy a diatomic molecule can possess a) translational kinetic energy b) rotational kinetic energy c) vibrational kinetic energy

The total internal energy of a diatomic gas can be written as:

$$\text{Total internal energy of a diatomic gas} = \text{Sum of translational kinetic energy of molecules} + \text{Sum of rotational kinetic energy of molecules} + \text{Sum of vibrational kinetic energy of molecules}$$

Experiments indicate that some diatomic molecules do not vibrate at room temperature. Their oscillations don't start until higher temperatures. For such molecules, only the translational and rotational energies contribute to the total energy of a molecule, at low temperatures. Nevertheless, all present types of average kinetic energy of the diatomic gas molecules are directly proportional to the temperature alone.

The exact relationship between gas temperature and average molecular kinetic energy becomes more complicated for larger molecules. This is because polyatomic molecules can vibrate in much more complex ways. Therefore, formulating a relationship between temperature and average molecular kinetic energy for a polyatomic gas is difficult, although it is known that internal energy is a function of only temperature for *all* ideal gases.

The simplest relationship is that of monatomic gases. The constant of proportionality for monatomic gases will now be determined.

Internal Energy of Monatomic Gases

Monatomic gases consist of molecules containing a single atom. If a single atom is taken as a point mass, the rotational kinetic energy of a molecule is zero; a point cannot rotate about itself.

The vibrational kinetic energy of a molecule is also zero, because there is no intramolecular bond to vibrate. The only contribution to the total kinetic energy of a molecule is from the translational kinetic energy, as shown in Figure 6.8.

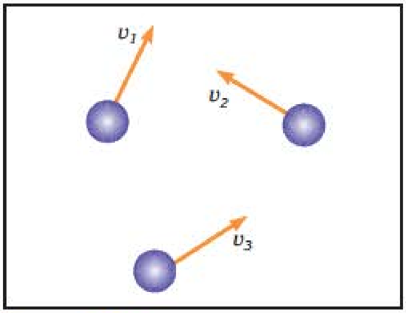


Figure 6.8 Molecules of a monatomic gas possess only translational kinetic energy

Therefore, the total internal energy of a diatomic gas sample can be written as:

$$\text{Total internal energy of a monatomic gas} = \text{Sum of translational kinetic energy of the molecules}$$

$$U_{\text{monatomic}} = N \times \left(\frac{1}{2}m_0\overline{v^2}\right) = N \times \left(\frac{3}{2}kT\right)$$

$$U_{\text{monatomic}} = \frac{3}{2}NkT = \frac{3}{2}nRT$$

Formulating an equation for diatomic gases is more difficult. A theorem from statistical mechanics called the 'equipartition theorem' is required. A short explanation of the equipartition theorem is included at the end of this chapter.

Exercise 6.6

Total energy from pressure and volume

What is the total internal energy of argon gas kept in a 1 lt flask under 2 atm pressure?

Solution

As argon is monatomic

$$U = \frac{3}{2}nRT$$

Since, neither the temperature nor the amount of gas is given, a different approach is required. Using the ideal gas equation

$$U = \frac{3}{2}PV$$

The product (PV) equals (nRT) for an ideal gas. Substituting the values with suitable units gives

$$U = \frac{3}{2}\left(2 \times 10^5 \mathrm{Pa}\right) \times \left(1 \times 10^{-3} \mathrm{m}^3\right)$$

$$U = 300\ \mathrm{J}$$

Exercise 6.7

Heat in an isovolumetric process

What amount of heat is needed to raise the temperature of 12 g of helium by 20 K at constant volume?

Solution

Helium gas is monatomic. Thus, the internal energy formula for monatomic gases can be used.

$$U = \frac{3}{2}nRT$$

To relate the internal energy change to temperature change, the energy formula for the initial and final cases are subtracted

$$\begin{array}{rl} & U_f = \frac{3}{2}nRT_f \\ - & U_i = \frac{3}{2}nRT_i \\ \hline & (U_f - U_i) = \frac{3}{2}nR(T_f - T_i) \end{array} \qquad \Delta U = \frac{3}{2}nR\Delta T$$

To calculate the heat transferred to the gas, the first law of thermodynamics is used

$$Q = \Delta U + W$$

Since volume is constant, W=0. Thus, the formula is

$$Q = \Delta U$$

$$Q = \frac{3}{2} nR\Delta T$$

12 g helium equals 3 moles.

$$Q = \frac{3}{2}(3)(8.31\ \mathrm{J/K})(20\ \mathrm{K})$$

$$Q \approx 748\,\mathrm{J}$$

Exercise 6.8

Heating monatomic and diatomic gases

Oxygen and helium samples containing the same number of moles are kept in two identical containers. The initial temperatures of the gases are equal, and both gases the absorb same amount of heat, at constant volume. Which gas will be hotter at the end?

Solution

Since both gases are heated at constant volume, W = 0 for both cases. All the absorbed heat energy is stored as internal energy of the gas. The internal energies of both gases increase by the same amount.

$$\Delta U_{O_2} = \Delta U_{He}$$

where ΔU represents the change in internal energy. The temperature changes of the gases will be different because helium is monatomic, while oxygen is diatomic.

$$\Delta T_{He} \neq \Delta T_{O_2}$$

Heat absorbed by helium gas is solely used for making helium molecules move faster.

$$Q = \Delta U_{He} = \Delta K_{\text{translation}}$$

Where ΔK represents the change in kinetic energy. The heat absorbed by the oxygen gas causes the oxygen molecules to move faster, rotate faster and oscillate faster.

$$Q = \Delta U_{O_2} = \Delta K_{\text{translation}} + \Delta K_{\text{rotation}} + \Delta K_{\text{vibration}}$$

Therefore, the same temperature change would require that oxygen absorbs a greater amount of energy.

Since the amounts of heat energies absorbed are equal, helium will be hotter at the end.

$$\Delta T_{He} > \Delta T_{O_2}$$

Note: Equipartition theorem and internal energy of diatomic gases

According to the equipartition theorem the average energy of each degree of freedom for a molecule equals $\frac{1}{2}kT$. The degree of freedom is the number of independent ways a molecule can possess energy. For example translational kinetic energy has three degrees of freedom along three axis:

$KE_{translational} = \frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{v_X^2} + \frac{1}{2}m\overline{v_Y^2} + \frac{1}{2}m\overline{v_Z^2} = 3\times\left(\frac{1}{2}kT\right) = \frac{3}{2}kT$. Rotational KE has two degrees of freedom; this is because the diatomic molecule can rotate about two axis (not counting the rotation about the axis along the molecule, since its energy is comparatively very low). Therefore, $KE_{rotational} = 2\times\left(\frac{1}{2}kT\right) = kT$. Vibrational KE also has two degrees of freedom (potential and kinetic energies of oscillations). Therefore

$KE_{vibrational} = 2\times\left(\frac{1}{2}kT\right) = kT$. The total energy of the molecule becomes:

$KE_{translation} + KE_{rotation} = \frac{3}{2}kT + kT = \frac{5}{2}kT$ at low temperatures and

$KE_{translation} + KE_{rotation} + KE_{vibration} = \frac{3}{2}kT + kT + kT = \frac{7}{2}kT$ at high temperatures.

Total internal energy of a diatomic gas sample is given by

$U_{diatomic} = \frac{5}{2}nRT$ or $U_{diatomic} = \frac{7}{2}nRT$ depending upon the temperature and the type of gas.

Summary

Definitions

Root-mean-square (rms) speed

$$v_{rms} \equiv \sqrt{\frac{v_1^2 + v_2^2 + \ldots + v_N^2}{N}}$$

Other Formulas

Average translational kinetic energy of gas molecules

$$\left(\frac{1}{2}m_0\overline{v^2}\right) = \frac{3}{2}kT$$

Average kinetic energy of gas molecules

$$KE_{average} = (const)\times T$$

The fundamental equation of kinetic theory

$$P = \frac{2}{3}n_u\left(\frac{1}{2}m_0\overline{v^2}\right)$$

Root-mean-square (rms) speed

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Total translational kinetic energy of an ideal gas

$$KE_{total} = \frac{3}{2}nRT$$

Total internal energy of a monatomic gas sample

$$U_{monatomic} = \frac{3}{2}NkT = \frac{3}{2}nRT$$

QUESTIONS AND PROBLEMS

(1 atm=100 kPa, g=10 N/kg, $N_A=6\times10^{23}$, $M_{He}=4$ g/mole)

6.1 Root Mean Square value

1. Five particles have velocities of 20 m/s, 30 m/s, 40 m/s, 50 m/s and 60 m/s. What is the rms speed of these particles?

2. The root- mean- square speed of molecules of helium gas is 500 m/s. What is the average kinetic energy of the gas molecules?

3. By what factor must we increase the rms speed of gas molecules, to increase the average kinetic energy of gas molecules by a factor of four?

6.2 The Pressure of an Ideal Gas

4. What are the assumptions of kinetic theory concerning an ideal gas?

5. What is the average kinetic energy of oxygen molecules under 1 Atm pressure, if the molecular concentration is $n_u = 2.5\times10^{19}\frac{1}{cm^3}$?

6. What is the pressure exerted by a gas, if the molecular concentration is $n_u = 3\times10^{25}\frac{1}{m^3}$ and the average kinetic energy of gas molecules is 10^{-20} J?

7. A sample of nitrogen gas contains 10^{20} nitrogen molecules in 1 cm^3 volume. The root-mean-square speed of nitrogen molecules is 500 m/s. What is the pressure of the gas? (M_{N_2}=28 g/mole)

8. By what factor does the pressure of a gas change when the rms speed of gas molecules is doubled, at the same concentration?

9. What is the rms speed of oxygen molecules, if the gas has a density of 1.2 kg/m^3, under 100 kPa pressure?

10. A 100-lt container holds 0.1 kg (5 moles) of neon gas at 120 kPa absolute pressure. What is the rms speed of neon molecules?

6.3 The Relationship between Temperature and Molecular KE

11. Two moles of helium is mixed with three moles of oxygen in a closed vessel. Which gas molecules have more kinetic energy on average, when the mixture reaches thermal equilibrium?

12. What is the average kinetic energy of helium molecules at 27 °C:

a) Under 1 atm pressure?

b) Under 5 atm pressure?

13. What is the average kinetic energy (=1/2 mv^2) of oxygen molecules at 27 °C under 1 atm pressure?

6.4 Root-Mean-Square Velocity

14. Two moles of helium is mixed with three moles of oxygen in a closed vessel. Which gas molecules move faster, on average, when the mixture reaches thermal equilibrium?

15. What is the rms speed of nitrogen molecules at 20 °C? (M_{N_2}=28 g/mole)

16. What is the ratio of the rms speed of helium molecules to the rms speed of nitrogen molecules at the same temperature? (M_{N_2}=28 g/mole)

17. A 0.05-kg gas sample is kept in a 20-lt container under 100 kPa pressure. What is the rms speed of the gas molecules?

6.5 Internal Energy of Gases

18. Explain why the internal energy of a gas sample cannot be changed without changing its temperature?

19. Which types of kinetic energy can a diatomic gas molecule have?

20. Consider 5 moles of helium (monatomic) and 5 moles of oxygen (diatomic) both at 800 K. Which gas sample has a greater total translational kinetic energy.

21. Consider 5 moles of helium (monatomic) and 5 moles of oxygen (diatomic) both at 800 K. Which gas sample has a greater internal energy?

22. What is the total internal energy of 20 g of helium at 300K?

23. What is the total internal energy of a 5 lt volume of argon gas under 120 kPa absolute pressure?

24. A sample of oxygen gas occupies 2 lt volume under 100 kPa pressure. What is the total translational kinetic energy of the gas?

25. The temperature of 2 moles of a monatomic gas increases from 20 °C to 300 °C. By how many joules does the internal energy of the gas change, if the temperature increase takes place:

a) At constant volume
b) At constant pressure

26. The volume of a monatomic gas sample increases by 4 lt, as heat is transferred to it under a constant pressure of 100 kPa. What is the change in the internal energy of the gas?

27. What amount of heat is needed to increase the temperature of 2 moles of a monatomic gas from 20 °C to 120 °C, at constant volume?

28. What amount of heat is needed to increase the temperature of 2 moles of a monatomic gas from 20 °C to 120 °C, at constant pressure?

29. Find an expression which describes the heat needed to increase the internal energy of n moles of a monatomic gas by ΔT:

a) At constant volume

b) At constant pressure

30. A 0.4-m^3 closed container holds neon at 27 °C under 100 kPa pressure. What amount of heat is needed to increase the temperature to 127 °C?

31. Internal energy of a monatomic gas sample increases by 120 J at constant pressure. What is the amount of heat transferred to the gas?

32. A monatomic gas sample, under constant pressure, is confined to a cylinder by a movable piston, and absorbs 600 J of heat. What is the change in the internal energy of the gas?

33. What amount of heat is needed to raise the temperature of 2 moles of a monatomic ideal gas by 200 °C, at constant pressure?

34. A monatomic gas sample kept in a 20-lt closed container absorbs 600 J of heat. By how many kilopascals does the gas pressure increase?

35. What amount of heat is needed to increase the pressure of neon gas, preserved in a sealed tube, of volume 500 cm^3, by 0.1 atm?

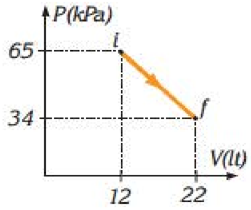
36. An 8-g helium sample is adiabatically compressed. During compression 300 J of work is done on the gas. By how many degrees does the gas temperature change?

37. During an adiabatic compression 83.1 J of work is done on a monatomic gas sample, which increases the temperature by 10 K. Find the number of moles of the gas.

38. A vertical cylinder-piston system holds a sample of monatomic gas. The piston has an area of 0.02 m^2 and a mass of 20 kg. Calculate the amount of heat that should be transferred to the gas, to lift the piston by 10 cm. Atmospheric pressure is 100 kPa.

39. Two containers, having respective volumes $V_1=1m^3$ and $V_2=2m^3$, hold air at $T_1=7$ °C and $T_2=27$ °C under $P_1=95$ kPa and $P_2=105$ kPa pressure. What are the common pressure and temperature when the containers are combined?

40. One mole of helium expands from (i) to (f) along the curve shown in the figure.

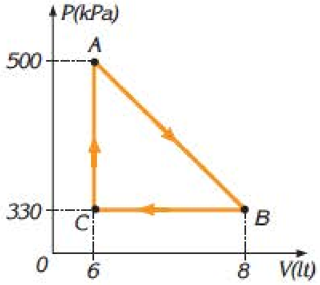


a) Find the resultant change in the internal energy of the gas

b) Find the net amount of heat transferred to the gas.

41. (This problem summarises the last six chapters.)

0.5 moles of a monatomic gas, undergoes the cyclic process shown in the figure.



a) Find the heat transferred to (or from) the gas along the processes A-B, B-C, C-A.

b) Find the efficiency of the cycle

CHAPTER 7

Real Gases

An ideal gas is a theoretical gas which can have any temperature and pressure. A real gas on the other hand, liquefies above a certain pressure, if its temperature is below a certain value called the 'critical temperature' of the gas.

7.1 PARTIAL PRESSURE

Dalton's law states that the pressure exerted by a mixture of gases equals the sum of the partial pressures of the gases in the mixture; the total pressure of two or more ideal gases enclosed in a container is the sum of the pressures each gas would apply if it were alone in the same container at the same temperature.

In other words, in case of gas mixtures; each gas applies a pressure as if it were alone in the container. This statement is hidden in the fact that, the ideal gas law makes reference to only the number of molecules applying pressure. The type of gas is unimportant.

Consider three different gases in a closed vessel, as shown in Figure 7.1. The total volume is available to all molecules. To calculate the pressure applied by each gas

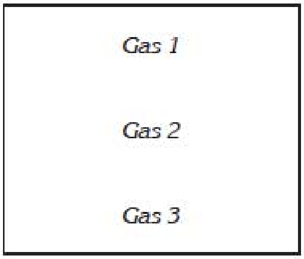


Figure 7.1 Each gas acts as if it were alone in the container

$$P_1V = n_1RT$$

$$P_2V = n_2RT$$

$$P_3V = n_3RT$$

Adding the equations gives

$$P_{total}V = n_{total}RT$$

Therefore, the pressure applied by gas 1 is given by;

$$\frac{P_1}{P_{total}} = \frac{n_1}{n_{total}}$$

$$P_1 = \frac{n_1}{n_{total}}P_{total}$$

7.2 SATURATED VAPOUR PRESSURE

The terms 'vapour' and 'gas' are different although both words refer to the same state of matter.

The term 'vapour' applies to the gaseous state of a substance that is normally found as a liquid at normal room temperature and pressure. Liquid water or liquid ethanol evapourates at room temperature to produce water vapour or ethanol vapour. On the other hand, nitrogen is always in a gaseous state under normal temperatures and pressure conditions, it is called a nitrogen gas (not nitrogen vapour).

Saturated Vapour Pressure

Consider a cylinder-piston system filled with pure water vapour. The dependence of pressure on the volume is shown in Figure 7.2.

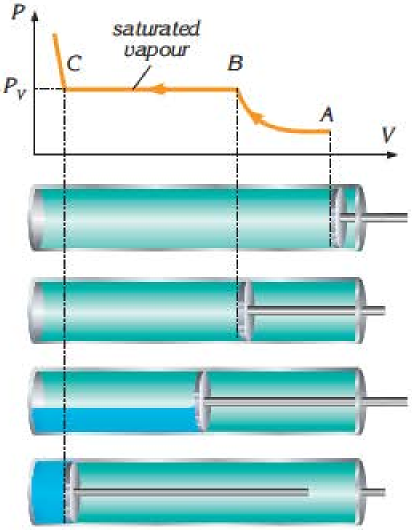


Figure 7.2 Pressure-volume curve during condensation

Between A and B: At low pressures, water vapour behaves like an ideal gas. Increasing the pressure applied by the piston, decreases the volume of the gas.

At point B: Vapour is saturated. This means vapour is about to condense.

Between B and C: Further decreasing the volume does not increase the pressure of the vapour, but saturated vapour starts to turn back into liquid.

At C: All vapour has condensed into an incompressible liquid.

The constant pressure indicated by (P_v) on the graph is called the '**saturated vapour pressure**' or simply the '**vapour pressure**'.

The name vapour pressure may be misunderstood. Vapour pressure is not pressure of vapour at any condition. It is the pressure of vapour just about to condense.

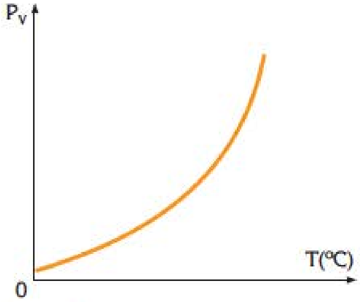


Figure 7.3 Vapour pressure of a substance depends only upon temperature. (The graph is that of water vapour)

Saturated vapour pressure of a compound depends only on temperature. As indicated in Figure 7.3. At a given temperature, the saturated vapour pressure is the maximum pressure that the vapour of a substance can have. If the pressure is increased at constant temperature, by compressing the vapour, it starts to condense.

At higher temperatures, saturated vapour pressure is higher, so a vapour sample can have higher pressures without turning into a liquid. This is because fast collisions between molecules, at high temperatures, tend to be elastic and molecules are less likely to stick together to form liquid drops.

As an example; the vapour pressure of water at 20 °C is 2.33 kPa, the vapour pressure of water at 100 °C is 100 kPa. In other words, the pressure of water vapour cannot be greater than 2.33 kPa at 20 °C.

Critical Temperature

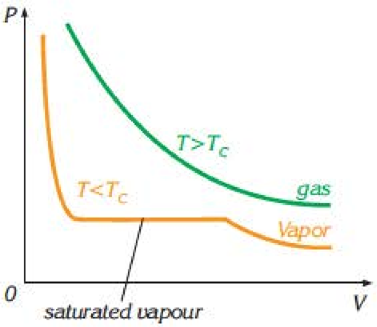


Figure 7.4 Above the critical temperature, condensation does not occur

When the temperature of a gas is above a certain value, - called the critical temperature of that substance - the gas does not turn into liquid, no matter how much the pressure is increased. The critical temperature for water vapour is 374.14 °C. The critical temperature for nitrogen gas is –146.9 °C. Thus nitrogen is not known as a vapour or a liquid under normal conditions of temperature and pressure. At room temperature (above - 146.9 °C), compressing a nitrogen sample, under high pressure does not result in liquid nitrogen. This is shown in Figure7.4. Above critical temperature, at high pressures the gas becomes denser, the properties of the gas and liquid phases are then the same, thus, above the critical temperature there is only one phase.

7.3 VAPOURISATION

Chapter 2 discussed the fact that, molecules in a liquid undergo transitions between temporary equilibrium positions. Just as molecular speeds of a gas have a distribution of values, liquid molecules also have different speeds due to thermal motion. If a molecule near the surface of a liquid has enough energy to break free from the molecular bonds, it escapes. This is shown in Figure 7.5.

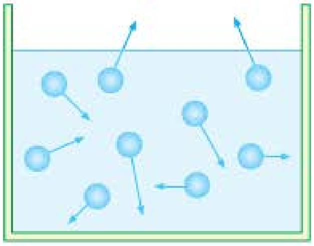


Figure 7.5 Vapourisation is the escape of high energy molecules from a liquid surface

Since fast molecules escape the liquid surface, (carrying away their kinetic energy), the internal energy of a liquid decreases due to vapourisation. If the liquid is isolated (allowing no heat transfer), the temperature decreases by vapourisation. This is because the liquid molecules take the energy required to vapourise from the liquid itself.

Our organs use this fact to keep our body temperature constant. Perspiration cools our body as it vapourises. During vapourisation, sweat drops absorb heat energy from the skin.

The rate of vapourisation is affected by various factors; temperature, surface area, type of liquid, and velocity of wind. Substances readily vapourising under standard conditions, (such as ether) are called volatile.

The vapourisation rate decreases with decreasing temperature, because the fraction of molecules having enough energy to vapourise decreases. Nevertheless, there are always molecules fast enough to escape. Vapourisation of a liquid continues at all temperatures, but at different rates.

Energy required to change the phase of unit mass of a substance from the liquid state to the gas state (latent heat of vapourisation) depends on the temperature. Since molecules of a liquid have more energy at high temperatures, less energy from outside is needed to break molecules apart from the molecular bonds in the liquid. For example, 1 g of water at 10 °C requires 590 cal heat energy to vapourise, whereas the same amount of water at 20 °C requires 585 cal.

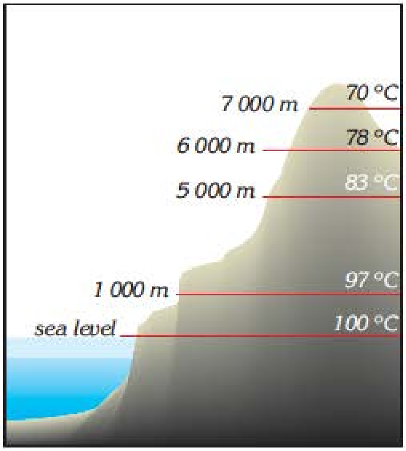


Figure 7.6 The change of boiling point with altitude

7.4 THE PROCESS OF BOILING

The process of boiling also means a phase change from the liquid state to the-vapour state. However, boiling and vapourisation are different. Vapourisation occurs at all temperatures, whereas, boiling occurs at a specific temperature, which is called the boiling point of a substance. The boiling point depends on the external pressure applied to the liquid.

Water boils at 100 °C, under 1 atm of external pressure. However, under 0.8 atm external pressure, boiling point decreases to 94 °C. Thus water is easier to boil on a mountaintop than at the seaside. However, this boiling water will not cook food, since it is not hot enough. The boiling points of water at various altitudes is shown in Figure 7.6.

Vapourisation occurs on the surface of a liquid. Energetic molecules, escaping the liquid - air boundary, form water vapour. Boiling occurs at all points throughout the volume of the liquid. Bubbles filled with water vapour may form deep beneath the liquid surface, as shown in Figure 7.7.

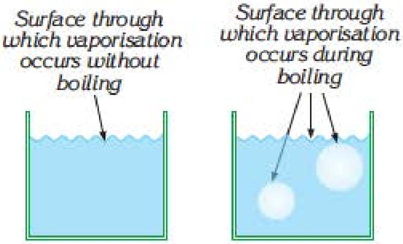

Surface through which vaporisation occurs without boiling
Surface through which vaporisation occurs during boiling

Figure 7.7 Vapourisation occurs on the surface of a liquid. Boiling occurs at all points throughout the volume of the liquid.

The formation of bubbles starts when many liquid molecules, energetic enough to break free from intermolecular bonds, incidentally move towards a point in the liquid.

To understand the relationship between boiling point and external pressure, consider a very small vapour bubble beginning to form under the surface of the water. Vapour inside the bubbles is saturated. If the pressure of the water vapour inside the bubble is at least equal to the external pressure, the vapour bubble may continue to expand. This is shown in Figure 7.8. This increasing volume, decreases the density of the vapour bubble; hence the bubble is lifted up by the buoyant force. Reaching the surface, bubbles burst with the familiar 'plop-plop' boiling sound.

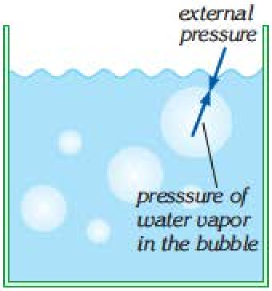


Figure 7.8 The bubble expands if $P_v = P_{external}$

Therefore, boiling means:

Vapour pressure of a liquid at a given temperature = External pressure on the liquid

Remember; the vapour pressure of the water depends only on the temperature of the water.

Hence there are two ways of boiling a liquid:

a) Increasing the pressure of the water vapour, by increasing the temperature of the water.

b) Decreasing external (atmospheric) pressure on the water. Generally the effect of the liquid pressure can be neglected when calculating the external pressure; since the atmospheric pressure is much greater.

Therefore, the boiling point of a liquid increases with increasing external pressure. This is the working principle of a pressure - cooker. Water boils at 100 °C under 1 atm pressure. In a pressure cooker, the boiling point of water rises to over 100 °C, due to the increased pressure. Hotter water makes the meal cook faster.

7.5 SATURATION

Consider a closed container filled with 'dry' air containing no water vapour in it. Therefore, the partial pressure of water vapour in air is initially zero.

If some water is placed in the container, water starts to evaporate. If the container is open to air, evaporation continues until no water is left. However, in the closed container, the amount of water does not decrease after a point. Has the evaporation stopped? The answer is no. Evaporation continues as long as molecules in the liquid continue to move.

As the liquid evaporates, the concentration of water molecules in the air increases. Since water molecules in the air move randomly in all directions, some molecules incidentally return to the liquid. After a point, the number of molecules escaping from the liquid surface, equals the number of molecules returning to the liquid. This situation is an example of 'dynamic equilibrium'. This is shown in Figure 7.9. When equilibrium is established, the amount of liquid water and the amount of water vapour in the container do not change.

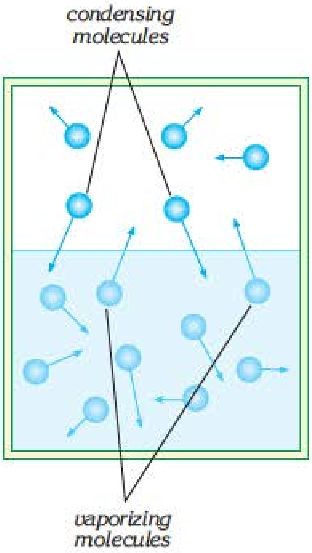
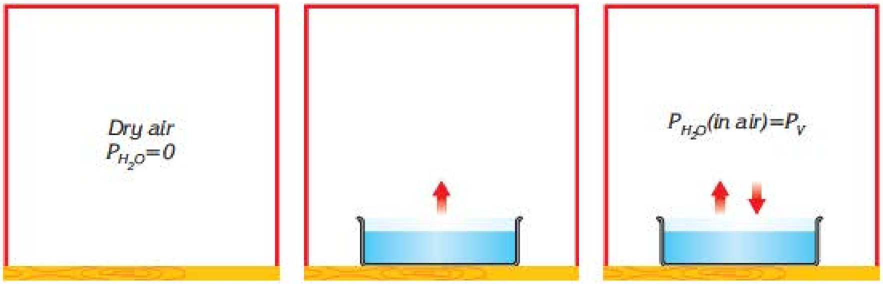


Figure 7.9 Vapour in equilibrium with its liquid state: the vapourisation rate equals the condensation rate

Once the equilibrium is established, we cannot increase the partial pressure of vapour in air at constant temperature. Decreasing the volume or adding vapour from outside just increases the rate of condensation above the rate of vapourisation, until equilibrium is reached once again. Therefore, at a given temperature, the partial pressure of vapour in air reaches its own maximum value, when vapour is in equilibrium with its own liquid state. Air cannot 'hold' any more vapour in it, at that temperature.

Since any added vapour readily condenses, the equilibrium vapour pressure at a given temperature is the saturated vapour pressure (Figure 7.10).



Initially air in the container is dry

Water vapourises, increasing the partial pressure of water vapour

Eventually, vapourisation and condensation rates are equal

Figure 7.10 Saturation means that the pressure of the water vapour in the air equals the vapour pressure of the water in the container.

In other words, 'saturation' means that the artial pressure of water vapour in air equals the saturatied vapour pressure of water at that temperature:

$$\text{Saturation} \leftrightarrow P_{H_2O}(\text{in air}) = P_v$$

7.6 RELATIVE HUMIDITY

Relative humidity (φ) is defined as the proportion of the partial pressure of water vapour in the air to the vapour pressure of water at that temperature;

$$\varphi_0 = \frac{P_{H_2O}\ (\text{in air})}{P_V}$$

Percent relative humidity is $\%\varphi = \varphi \times 100$.

Therefore $\varphi = 1$ for saturation. Since saturation means air can not carry any more water vapour, dew starts to form at $\varphi = 1$.

The relative humidity can be increased in two ways:

a) The amount of water vapour in the air is increased (by vapourising more water)

b) Saturation vapour pressure (P_V) is decreased, by decreasing the temperature.

This is why dew forms in the morning (when it is cold), or on cold surfaces (such as window panes). Cold air cannot 'carry' water vapour in it.

Exercise 7.1 The mass of water vapour

a) What is the partial pressure of water vapour in air at 20 °C, if the relative humidity is 40%? The vapour pressure of water at 20 °C is $P_V = 2333$ Pa.

b) Under these conditions, find the mass of vapour in air in a 100 m^3 room.

c) How much additional water can be vapourised in the same room?

Solution

a) 40 % relative humidity means $\varphi=0.4$

Using the definition of relative humidity

$$\varphi = \frac{P_{H_2O}(\text{in air})}{P_V}$$

$$P_{H_2O}(\text{in air}) = \varphi P_v$$

$$P_{H_2O}(\text{in air}) = 0.4 \times (2333\text{ Pa})$$

$$P_{H_2O}(\text{in air}) = 933.2\text{ Pa}$$

b) Treating water vapour in air as an ideal gas

$$P_{H_2O}(\text{in air})V = n_{H_2O}(\text{in air})RT$$

$$n_{H_2O} = \frac{P_{H_2O}V}{RT}$$

$$n_{H_2O} = \frac{(933.2\text{Pa})(100\text{m}^3)}{(8.31\text{J/K})(293\text{K})}$$

$$n_{H_2O} = 38.3\text{ moles}$$

$$m_{H_2O} = n_{H_2O}\, M_{H_2O}$$

$$m_{H_2O} = (38.3\text{moles})(18\text{ g/mole})$$

$$m_{H_2O}(\text{in air}) \approx 690\text{ g}$$

c) To determine the additional amount of water that can be vapourised, calculate the maximum (saturation) amount of water that the air can 'carry'.

$$P_V V = n_{sat}RT$$

$$n_{sat} = \frac{P_V V}{RT}$$

$$n_{sat} = \frac{(2333\text{ Pa})(100\text{ m}^3)}{(8.31\text{ J/K})(293\text{ K})}$$

$$n_{sat} = 95.8\text{ moles}$$

$$m_{sat} \approx 1725\text{ g}$$

1725 g vapour is the maximum amount that can be carried in 100 m^3 air at 20 °C.

Therefore 1725 g – 690 g = 1035 g of additional water can be vapourised in the room.

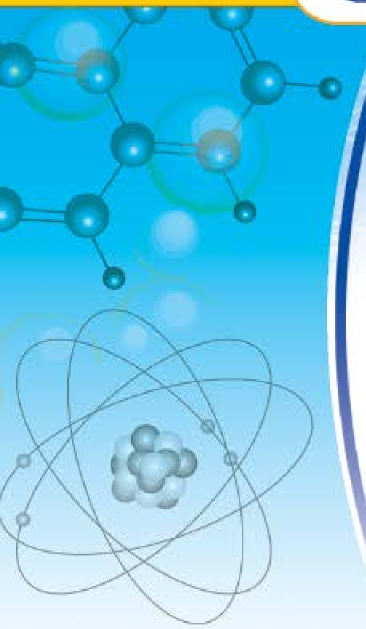
Note that proportions could also have been used for part (c).

40 % humidity ⇒ 690 g vapour

100 % humidity ⇒ 1725 g vapour

at the same temperature.

Summary



Definitions

Above **critical temperature**, a gas does not turn into liquid, no matter how much the pressure is increased.

Vapour pressure (or saturated vapour pressure) is the pressure of vapour just about to condense.

Saturation means that the partial pressure of water vapour in air, equals the vapour pressure of water at a given temperature

Saturation: $P_{H_2O}(\text{in air}) = P_v$

Relative humidity (φ) is the proportion of the partial pressure of water vapour in the air to the vapour pressure of water at that temperature

$$\varphi = \frac{P_{H_2O}(\text{in air})}{P_v}$$

Laws and Principles

Saturated vapour pressure of a compound depends only on temperature.

Partial pressure of a vapour in air, at a given temperature, cannot exceed the vapour pressure of its liquid at that temperature.

Boiling starts when the vapour pressure of a liquid equals the external pressure up on the liquid.

Other Formulas

Partial pressure: $P_1 = \frac{n_1}{n_{total}} P_{total}$

QUESTIONS AND PROBLEMS

7.1 Partial Pressure

1. Explain the term 'partial pressure'.

2. What is Dalton's law concerning the partial pressure of a gas in a mixture?

3. Air is a mixture of different gases. It is composed of 78% nitrogen, 21 % oxygen, 1% water vapour, carbon dioxide, argon and other gases. What is the partial pressure of oxygen when the air pressure is 1 atm?

4. A sealed vessel holds equal masses of helium and oxygen at 27 °C, under 100 kPa pressure. What is the density of the gas mixture? ($M_{He}=4$ g/mole, $M_{O_2}=32$ g/mole)

7.2 Saturated Vapour Pressure

5. What is the difference between the terms 'gas' and 'vapour'?

6. Explain the term 'saturated vapour pressure'.

7. What is the difference between 'pressure of water vapour in air' and 'saturated vapour pressure of water'? Which is a physical constant?

8. How can the saturated pressure of water be changed?

9. What does 'critical temperature' mean?

7.3 Vapourisation

10. Which factors determine the rate of vapourisation?

11. Why does the temperature of an isolated liquid drops as it vapourises?

12. Suppose we place a glass of water in a closed room. Does the room temperature change as the water vapourises?

13. Water at 0 °C partly fills a closed container. What percent of water in the container turns into ice, if the air in the container is pumped out? (Take L_v =595 cal/g for water at 0 °C, L_f=80 cal/g)

7.4 The Process of Boiling

14. What are the two characteristic differences between vapourisation and boiling?

15. What is the density of water vapour in an air bubble rising to the surface of boiling water under standard atmospheric pressure? (P_0=100 kPa)

16. Why does the temperature remain constant during boiling?

17. What is the definition of 'boiling' in terms of the external pressure and vapour pressure of the liquid?

18. Why does the boiling point increase with increasing external pressure?

19. Water can be boiled by increasing its temperature. Is there any other way of boiling water?

7.5 Saturation

20. Define 'saturation'

21. Saturated water vapour is contained in a cylinder-piston system. Which of the following actions will increase the pressure of the saturated vapour in the cylinder?
    a) Increasing the external pressure by applying more force on the piston
    b) Adding more water vapour at constant volume
    c) Increasing the temperature

22. Explain why the saturated vapour pressure at a given temperature is the maximum pressure the vapour can have at that temperature?

23. Suppose air is saturated with water vapour.

a) What happens if some more water is added (i.e. by boiling some water) this room?

b) What happens if we decrease the temperature of the room?

24. Explain why dew formation takes place in the mornings and on colder surfaces?

7.6 Relative Humidity

(M_{H_2O}=18 g/mole)

25. Define relative humidity.

26. How does the relative humidity affect the rate of vapourisation?

27. Describe two ways of increasing the relative humidity in a room.

28. Find the partial pressure of water vapour in air at 25 °C, if the relative humidity is 60%. (The vapour pressure of water at 25°C is P_v=3 170 Pa)

29. What is the mass of water vapour in air in a 200 m^3 room, if the temperature is 25 °C and the relative humidity is φ=0.6. (Take P_v=3 170 Pa at 25 °C)

30. How much additional water can be vapourised in a 200-m^3 room without forming dew, if the temperature is 25 °C and the relative humidity is φ=0.6. (Take P_v=3 170 Pa at 25 °C)

31. The relative humidity in a closed vessel of 0.5 m^3 volume is 60% at 20 °C. How much additional water can be vapourised in this vessel, if the saturated vapour pressure at this temperature is 2 333 Pa?

32. A cylinder-piston system contains pure unsaturated water vapour. Describe two methods of saturating the vapour, without adding vapour from the outside.

33. A cylinder-piston system contains 0.3 moles of pure water vapour. The initial volume and temperature are 20 °C and 0.57 m^3.

a) Keeping the temperature constant, at what volume is the vapour saturated? (Take P_v=2 333 Pa at 20 °C)

b) Show that by keeping the volume constant, the vapour in the cylinder becomes saturated at 10 °C. (Take vapour pressure as P_v=1 238 Pa at 10 °C)

34.

A horizontal cylinder-piston system contains 0.2 moles of water vapour at 50 °C. (Take P_v=12.3 kPa at 50 °C). What is the pressure of water vapour in the cylinder?

a) When the volume is 0.05 m^3

b) If the volume is decreased to 0.04 m^3 isothermally

c) If the volume is decreased to 0.03 m^3 isothermally

35.

A horizontal cylinder-piston system contains 0.2 moles of water vapour at 50 °C. The initial volume of vapour is 0.05 m^3. What mass of liquid water condenses in the cylinder, if the volume is isothermally decreased to 0.01 m^3? (Take P_v=12.3 kPa at 50 °C

36. Water at 20 °C is placed under a movable piston in a cylinder of 30 cm^2 area. What mass of water vapourises when the piston is raised by 10 cm? (Take P_v=2 333 Pa at 20 °C, T=const)

37. Relative humidity is 60% in the evening when temperature is 15 °C. Temperature drops to 5 °C at night. Will dew formation take place? (The vapour pressure of water at 15 °C and 5 °C are 1.71 kPa and 0.87 kPa, respectively)

38. At 10 °C, the relative humidity of air in a closed container is 50%. What is the relative humidity at 30 °C? (Vapour pressure of water at 10 °C and 30 °C are 1.23 kPa and 4.25 kPa, respectively)

39. Absolute humidity is defined as the amount of water vapour per unit volume. What is the absolute humidity of air at 15 °C, if the relative humidity is 80%? The vapour pressure of water at 15 °C is P_v=1.71 kPa.

40. The vapour pressure of water at T=36 °C is (approximately) P_v=6000 Pa. Find the total mass of V=1m^3 of humid air, if its pressure is P=100 kPa, and its relative humidity is 50%. (Take molar mass of dry air to be M_{air}=29 g/mole and the molar mass of water M_{water}=18 g/mole)

(Hint: Total mass in 1 m^3 is the mass of dry air in 1 m^3 plus the mass of water vapour in 1 m^3)

41. The volumes and relative humidity values of air in two vessels are V_1= 2 m^3, V_2= 3 m^3 and φ_1= 20%, φ_2 = 40%, respectively. Find the common relative humidity when the vessels are combined. Assume that temperature does not change.

CHAPTER

8

Liquids and Solids

The behaviour of a substance in response to the action of an external force determines the mechanical properties of that substance. It is possible to explain the mechanical properties of matter using simplified physical models. The nature of interactions between the molecules of a substance gives that substance its unique characteristics. Strong intermolecular bonds make a solid resist the deforming effect of external forces. A liquid is practically incompressible, but cannot preserve its shape against the action of an external force. In this chapter, the mechanical properties of liquids and solids will be discussed.

8.1 SURFACE TENSION

A pencil dipped in mercury and then in water comes out dry from one liquid, but wet from the other*. Hot water and soap are needed to clean clothes well. On a hot summer day insects can be observed walking over the surface of a pond, as if they didn't know Archimedes's principle. Such diverse phenomena can be explained in terms of forces between molecules (inter-molecular forces).

Liquids, naturally, try to achieve the smallest surface area to volume ratio. Drops of mercury are seen to take on a spherical form (a sphere has the smallest surface with respect to its volume). Drops of water on a glass surface, try to take on such a form, but generally gravity and the attractive forces of glass, molecules are stronger than forces between water molecules. Nevertheless, a freely falling water drop is more or less spherical.

This fact can be explained by considering the forces on the water molecules. Each molecule in a water sample is attracted by the other water molecules surrounding it. For molecule A in Figure 8.1, the net force is zero, as it is attracted by all sides. For the surface molecule B there is a net inward force. These inward forces all over the surface make a liquid drop spherical.

The surface of a liquid forms a thin layer, like a film coating the liquid. It is possible to balance a pin on the curved surface of a brimming glass of water. This is shown in Figure 8.2. The liquid surface tries to shrink to the smallest surface area possible.

To perform a quantitative analysis of surface forces, a parameter called surface tension is defined.

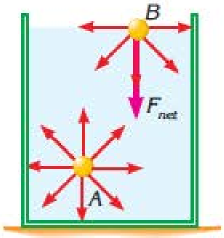


Figure 8.1 Forces on a surface molecule and an interior molecule

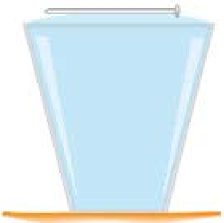


Figure 8.2 Surface tension keeps the needle afloat

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* Don't try this. Mercury is poisonous and easily vapourises.

Consider the rectangular wire frame in Figure 8.3. One side is free to slide in both directions, as shown in Figure 8.3. The frame is dipped in water, which forms a film stretching over the structure.

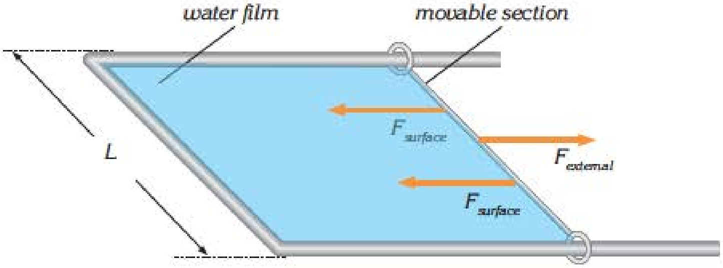


Figure 8.3 A rectangular wire frame demonstrates surface tension.

In the absence of an external force, the film - trying to reduce the surface area - pulls the movable side back, until the surface area is nearly zero. In the figure two forces are indicated by the liquid film, since the liquid has two surfaces, as shown in Figure 8.4.

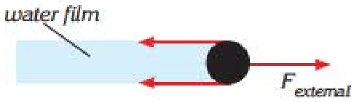


Figure 8.4 Water film has two surfaces, hence two surface tension forces act on the movable section.

The surface tension is defined as the ratio of the surface-tension force to the length, L along which it acts. Greek letter (sigma) symbolises the surface tension.

$$\sigma = \frac{F}{L}$$

Surface tension has the dimensions of force per unit length. The SI unit for surface tension is $\frac{N}{m}$.

The surface tension of liquids decreases with increasing temperature, as shown in Table 8.1. This is why detergent is used along with hot water for washing clothes. Both factors decrease the surface tension of water, so water can pass through the small holes of the fabric easily.

The reduction of surface tension with increasing temperature can be explained in terms of molecular interactions. Surface tension arises from intermolecular attractive forces, and a higher kinetic energy of molecules, indicated by increasing temperature, diminishes the effects of these forces.

Substance	Surface tension, at 20°C (N/m)
Benzene	0.029
Glycerin	0.063
Mercury	0.465
Water	0.072
Water 100°C	0.059

Table 8.1 Surface tensions of various liquids.

The surface tension force is not an elastic force. For the wire frame above, surface tension force does not increase, but rather stays constant as the water film is stretched.

The expression for the surface-tension force shows us that the force is independent of amount of stretching.

$$F = \sigma L$$

8.2 ADHESIVE AND COHESIVE FORCES

Forces between like-molecules (e.g. water-water) are called cohesive forces.

Forces between unlike-molecules (e.g. water - glass) are called adhesive forces.

When adhesive forces are greater than cohesive forces, for a liquid, in contact with a surface, the liquid 'wets' the surface. If cohesive forces are greater, the surface is not wetted.

Material	Interface	Angle of contact
Water	Glass	0°
Water	Paraffin	107°
Mercury	Glass	140°

Table 8.2 Contact angles of various liquid interfaces

It is possible to compare adhesive and cohesive forces by observing the angle of contact between the liquid and the solid surface. Figure 8.5 shows the angle of contact (ϕ) of the water-air interface, against two different surfaces. The angle of contact is defined as the angle between the liquid and solid surfaces, facing the interior of the liquid.

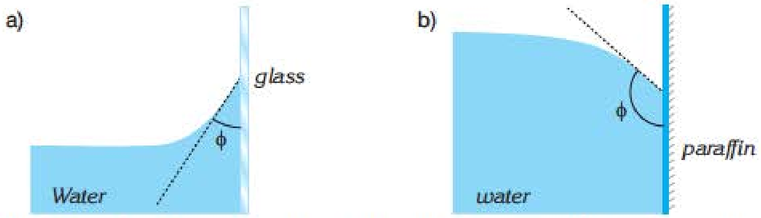


Figure 8.5 Angle of contact between two different interfaces. a)Adhesive F > Cohesive F, b) Cohesive F > Adhesive F

- Adhesive forces > Cohesive forces ⟷ $\phi < 90°$ ⟷ Liquid tries to climb upwards along the solid surface. Liquid gas interface curves upwards, as shown in Figure 8.5a.
- Adhesive forces = Cohesive forces ⟷ $\phi = 90°$ ⟷ Liquid stays horizontal.
- Adhesive forces < Cohesive forces ⟷ $\phi > 90°$ ⟷ Liquid tries to shrink into a sphere. Liquid glass interface curves downward, as shown in Figure 8.5b.

8.3 CAPILLARY ACTION

A capillary is a tube with a very small internal diameter. Capillary action is the rise or fall of a liquid in a capillary, as shown in Figure 8.6.

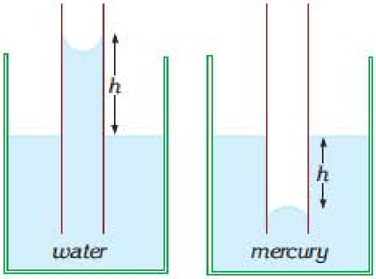


Table 8.6 Capillary action

Absorption of water by a paper towel is an example of capillary action. Paper pulls water into the narrow channels between the fibers. Capillary action also contributes to the raising of water along a tree from roots to leaves.

The capillary effect is more significant in thinner tubes, as shown in Figure 8.7.

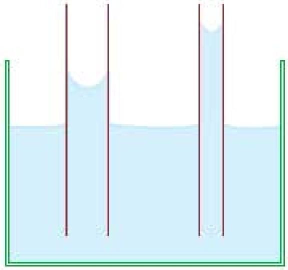


Table 8.7 The capillary effect is more significant in thinner tubes

A quantitative expression for the height of water in a glass tube will now be found.

Consider the thin long tube in Figure 8.8. The weight of the water column above the water surface is supported by the surface tension force.

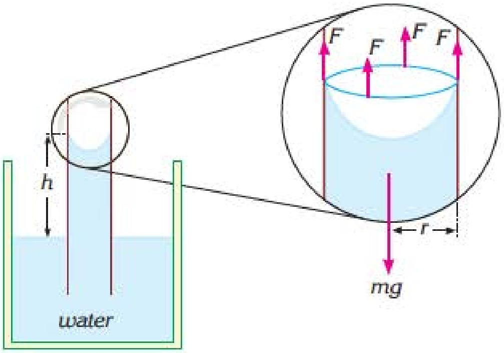


Figure 8.8

The angle of contact between water and the clean glass is nearly zero. Thus, the surface tension force can be taken as being directed upwards; the horizontal components cancel, as shown in Figure 8.9.

The equilibrium condition becomes;

$$\text{Weight of the water column over the water surface} = \text{Total upward force of the surface tension}$$

$$mg = \sigma L$$
$$\rho V g = \sigma L$$
$$\rho(\pi r^2 h)g = \sigma(2\pi r)$$

Cancelling and rearranging gives

$$h = \frac{2\sigma}{\rho g r}$$

In the solution above, the contact angle is zero, so we did not have to deal with components. In cases where the contact angle is not small, the formula for liquid height, as shown in Figure 8.9, becomes

$$h = \frac{2\sigma}{\rho g r}\cos\theta$$

The angle of contact is determined by the properties of the solid, the liquid and the gas at the interface. In Table 8.2, the gas interface is air.

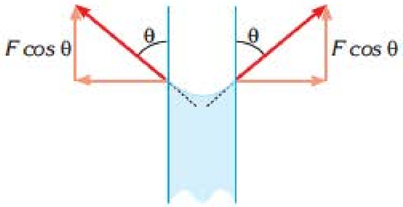


Figure 8.9 Only the surface tension component acting upwards is included. The horizontal components cancel.

8.4 SURFACE POTENTIAL ENERGY

Consider, once again, the water film stretching over the rectangular frame with one movable side. Suppose the movable portion is pulled, enlarging the surface area with a force equal to the surface tension force. The net force is zero, the wire moves with constant velocity.

The work done in pulling the sliding portion from position 1 to position 2 must have been stored as a kind of potential energy change, since no other known energy form appears (Figure 8.10).

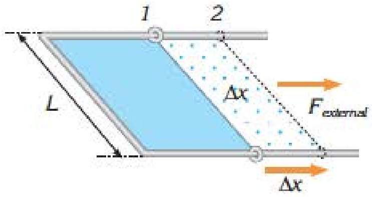


Figure 8.10 Work done by an external force is stored as the potential energy of the surface

A surface potential energy U, can be defined. Following the discussion above, change in surface potential energy (ΔU) is;

$$W_{\text{external}} = \Delta U_{\text{total}}$$
$$F_{\text{external}}\Delta x = 2\Delta U \text{ (two surfaces)}$$

Inserting $F_{\text{external}} = 2\,F_{\text{surface tension}}$ gives

$$2F\Delta x = 2\Delta U$$
$$(\sigma L)\Delta x = \Delta U$$

However, $L\ \ \Delta x$ equals the area change ΔA;

$$\sigma\Delta A = \Delta U$$

The expression describes the change in surface potential energy. Surface potential energy can be defined as follows:

$$U_{surface} = \sigma A$$

Checking the unit consistency;

$$[J]=\left[\frac{N}{m}\right]\left[m^2\right]$$

Example 8.1

Height of a water column

A long glass tube, open at both ends, has its end partly dipped into water. What is the inner radius of the tube, if the water in the tube rises to a height of 1 cm above the surface of the water?

Solution

The surface tension for water in contact with glass is (from Table 8.1)

$$\sigma_{water} = 0.072 \text{ N/m.}$$

Using the height formula for capillary action gives;

$$h=\frac{2\sigma}{\rho g r}$$

$$r=\frac{2\sigma}{\rho g h}$$

$$r=\frac{2\,(0.072\text{ N/m})}{(10^3\text{ kg/m}^3)(9.8\text{ N/kg})(0.01\text{ m})}$$

$$r\approx 1{,}5\times10^{-3}\text{ m}$$

The inner radius of the tube is approximately 1.5 mm.

8.5 THE EXCEPTIONAL BEHAVIOR OF WATER

Most substances expand as they melt. Water is a significant exception to this rule. The volume of ice decreases, as it turns into water. Hence water is denser than ice. This is why ice floats on the surface of water.

If water behaved like most other substances, ice would be denser than water. In that case, lakes and seas would start freezing from the bottom, rendering aquatic life (and hence all life on the planet) impossible.

The volume of water decreases with increasing temperature between 0 °C and 4 °C. Water reaches its smallest volume and highest density at 4 °C. Above this temperature the volume of water starts to increase with increasing temperature, as shown in Figure 8.11.

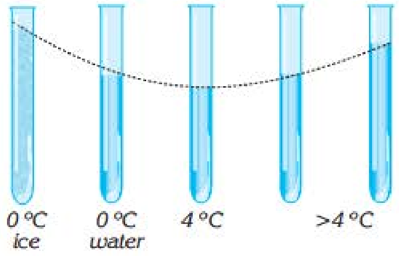


Figure 8.11 Water is densest at +4 °C

Since its density increases between zero and 4 °C, reaching its maximum value at + 4 °C, the water temperature at the bottom of a lake is +4 °C, irrespective of the temperature outside. The ice layer between the water and air serves as a perfect insulator, preventing heat loss from water. As the air gets colder, the thickness of ice inceases, providing better insulation, as shown in Figure 8.12.

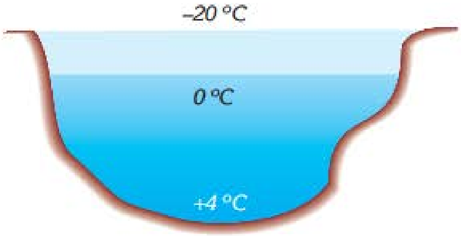


Figure 8.12 The temperature at the bottom is not affected by the outside temperature.

For the water at the bottom to cool down below +4 °C, all the water in the lake must have been cooled to this temperature. However, the winter does not last long enough to allow this much heat loss. Hence the fish can survive even the coldest winter.

8.6 THE MOLECULAR STRUCTURE OF SOLID SUBSTANCES

Bonds between molecules of solids are stronger than liquids and gases. A molecule in a solid structure is not free to move around in the substance.

The arrangement of atoms forming the solid structure differs between substances. The atoms of crystalline solids are neatly arranged. In an amorphous solid, however, atoms are just lumped together.

Crystalline Solids

A crystalline structure is characterised by two properties:

- Regularly repeating internal structure
- External plane faces

Atoms are invisible, but the regular internal structure of a snow crystal is apparent from its visible form. The structure of an ice crystal is shown in Figure 8.13. Close examination of a salt grain reveals its planar surfaces , as shown in Figure 8.14. All crystals of the same substance have the same angles between their faces.

The arrangement of atoms in a regular periodic pattern, in three dimensions, is called the crystal lattice.

A group of atoms that repeats in three dimensions, in the crystal structure, is called a unit cell. Crystalline substances are classified into seven systems on the basis of the geometry of their unit cells. The cubic system is one of these seven systems. The possible arrangements of a cubic system are shown in Figure 8.15.

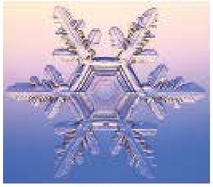


Figure 8.13 A snow crystal

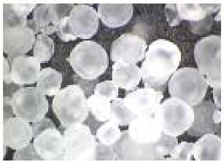


Figure 8.14 Salt grains

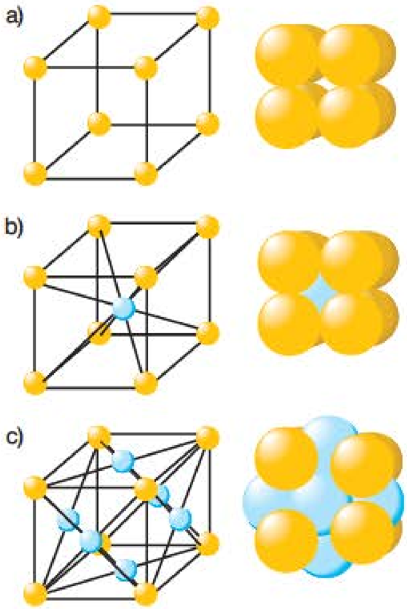


Figure 8.15 Three possible packings for cubic crystals a) Simple cubic b) Body-centred c) Face-centred

An element can exist in two or more distinct physical forms. The phenomenon is known as allotropy. As an example, carbon displays allotropy in graphite and diamond, which means both the substances graphite and diamond consist of carbon atoms, however, they display totally different properties. These allotropic structures are shown in Figure 8.16

Different arrangements of the atoms in the crystals cause allotropic forms to differ in physical properties; such as colour, density, hardness, conductivity etc.

Physical properties (e.g. mechanical strength, heat and electric conduction) of crystalline solids, depend upon the direction of flow within the lattice. Such substances are called anisotropic.

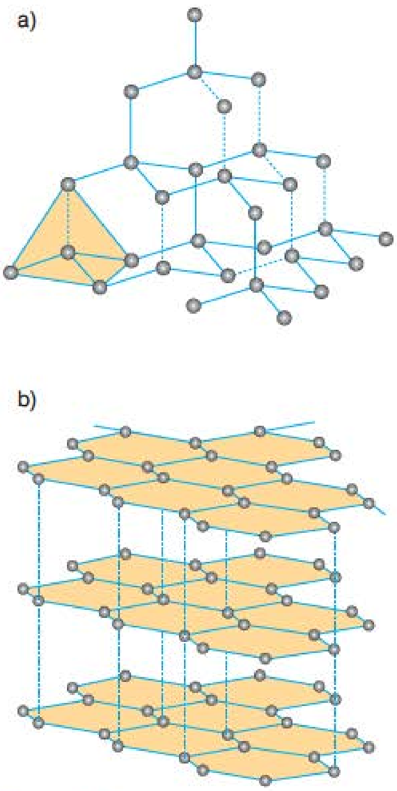


Figure 8.16 Carbon displays allotropy in: a) diamond b) graphite

Polycrystalline Solids

Metals have a crystalline structure. However, examining a piece of metal, its crystalline structure is apparent, neither in its physical properties (metals under normal conditions are isotropic) nor in its appearance (no necessarily flat surfaces). Therefore crystalline materials need not necessarily exist as crystals.

Metals are composed of a large number of small crystals. The properties of each crystal unit depend upon the direction, however, these units are irregularly oriented in the structure. As a result, for volumes much greater than the volume of a single crystal, all directions in the metal are equivalent and the properties of metals are also equivalent in all directions.

Metals are not the only example of polycrystalline solids. A piece of sugar, for example, has a polycrystalline structure.

Amorphous Solids

Amorphous solids do not have any order in the arrangement of their atoms. Only proximate atoms have some order. The recurrence of the same structure in all directions, which is characteristic of crystals, is not present in amorphous substances. Plastic, tar, resin, and glass are examples of amorphous solids. Amorphous substances are isotropic; their physical properties are independent of direction within the solid.

Frequently the same substance (such as quartz) may occur both in crystalline and amorphous forms.

The amorphous substances occupy an intermediate state between crystalline solid structures and fluids. They behave like elastic solids against sudden shocks, but flow like liquids over very long time scales.

Crystalline solids have definite melting points. Amorphous solids do not have a definite melting point. In other words, changing the shape of an amorphous substance gets easier as temperature increases. At high temperatures, an amorphous solid becomes more like a very thick (viscous) liquid. However, since the transformation takes place gradually, a single temperature cannot be identified as the melting point.

8.7 STRESS AND STRAIN, ELASTICITY, YOUNG'S MODULUS

Consider a metal bar of length, L and cross sectional area, A. The bar is fixed at one end and a force F is applied at the other end, compressing or stretching the bar. Figure 8.17 indicates this scheme. Under the action of a force, length changes by ΔL.

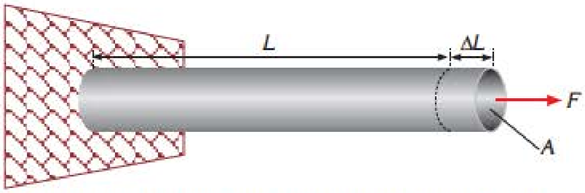


Figure 8.17 A metal bar elongates under the action of tensile force

Strain is the fractional change in length:

$$\text{Strain} = \frac{\text{Change in length}}{\text{Initial length}}$$

$$\varepsilon = \frac{|\Delta L|}{L}$$

Mechanical stress is the (perpendicular) force to cross-sectional area ratio:

$$\text{Stress} = \frac{\text{Force}}{\text{Area}}$$

$$\sigma = \frac{F}{A}$$

Mechanical stress is dimensionally equivalent to pressure. The unit of stress is

$$\frac{N}{m^2} = Pa.$$

The type of mechanical stress, elongating the substance is called the tensile stress. Increasing the tensile stress on a substance increases its length.

A typical tensile stress versus strain curve is given in Figure 8.18:

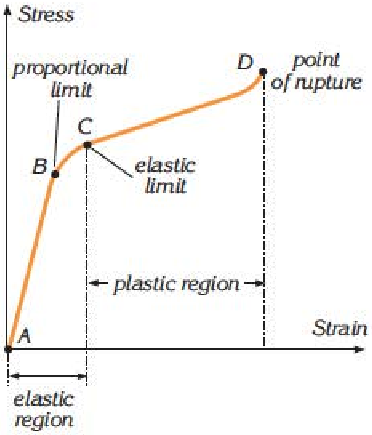


Figure 8.18 A typical strain-tensile stress curve

In the elastic region of the curve (between points A and C), the material returns to its initial length when the stress is removed.

If the elastic limit (point C) is exceeded, the substance becomes permanently deformed (between C and D); it does not assume its initial shape, even after the stress is removed. Such a deformation is called plastic deformation.

If mechanical stress is further increased, the material breaks at point D.

As seen from the curve, strain is proportional to mechanical stress for small strain values, from A to B. Therefore, for sufficiently small strain

$$\frac{\text{Tensile Stress}}{\text{Tensile Strain}} = \text{Constant}$$

Material	Young's modulus (N/m^2)
Aluminum	7.0×10^{10}
Gold	8.0×10^{10}
Steel	20×10^{10}

Table 8.3 Young's moduli for various substances

The constant in the formula is called Young's modulus, and is denoted by E. Thus

$$\frac{F/A}{\Delta L/A} = E$$

Young's modulus depends only on the substance, not on the geometry or size. Therefore, it is a characteristic property for a solid. Since stress is a dimensionless quantity, the dimension of Young's modulus is the dimension of mechanical stress, which is $[\text{Force}/\text{Area}]$. Young's moduli for various substances are listed in Table 8.3.

8.8 HOOKE'S LAW

The previous section showed that strain is proportional to stress; within the elastic limit of a substance. Thus

$$\text{Stress} = \text{Constant} \times \text{Strain}$$

for sufficiently small strain values. This relationship is known as Hooke's law. Hooke's law can be written for a given object using Young's modulus

$$\frac{F}{A} = E\frac{\Delta L}{L}$$

$$F = \left(\frac{EA}{L}\right)\Delta L$$

Since for a given substance Young's modulus, cross sectional area and original length are constants,

$$\text{Force} = \text{Constant} \times \text{Elongation}$$

$$F = kx$$

which, is already familiar.

Example 8.2 Elongating a steel wire

What force is needed to increase the length of a steel wire by 4 mm? The initial length of the wire is 2 m and its cross sectional area is 0.5 mm^2.

Solution

From Hooke's law;

$$F = \left(\frac{EA}{L}\right)\Delta L$$

Using Young's modulus for steel from Table 8.3

$$F = \frac{(20\times10^{10}\,\text{Pa})(0.5\times10^{-6}\,\text{m}^2)}{2\text{m}}(4\times10^{-3}\,\text{m})$$

$$F = 200\ \text{N}$$

Summary

Definitions

The **surface tension** is the ratio of the surface-tension force to the length L, along which it acts.

$$\sigma = \frac{F}{L} \qquad \text{unit} : \frac{N}{m}$$

Cohesive forces are forces acting between like molecules. **Adhesive forces** are forces acting between unlike molecules.

Strain is the fractional change in length:

$$\varepsilon = \frac{|\Delta L|}{L}$$

Mechanical stress is (perpendicular) force to cross-sectional area ratio:

$$\sigma = \frac{F}{A} \qquad \text{unit} : \frac{N}{m^2}$$

Young's modulus

$$\frac{F/A}{\Delta L/L} = E$$

Laws and Principles

Hooke's Law (for sufficiently small strain)

$$\text{Stress} = \text{Constant} \times \text{Strain}$$

Other Formulas

Height of liquid column in capillary

$$h = \frac{2\sigma}{\rho g r}$$

Surface potential energy

$$U_{\text{surface}} = \sigma A$$

QUESTIONS AND PROBLEMS

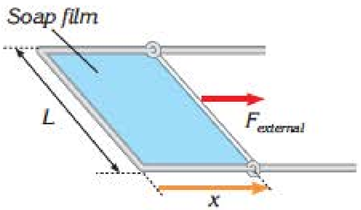
(Take $\sigma_{water}=0.072$ N/m, $\sigma_{mercury}=0.465$ N/m, $g=10$ N/kg, $\rho_{water}=1000$ kg/m^3)

8.1 Surface Tension

1. Define surface tension. What is the SI unit for surface tension?

2. Why do we use hot water and detergent for washing clothes?

3.



Consider the soap film stretched over a frame as in the figure. Do we need to increase the force $F_{external}$ in the figure, as the distance indicated by x increases?

8.2 Adhesive and Cohesive Forces

4. Define an 'adhesive force' and a 'cohesive force'.

5. What is the condition for a liquid to 'wet' a solid surface?

6. Explain why a wetting liquid takes on a concave form in a capillary tube, while a non-wetting liquid takes on a convex shape?

8.3 Capillary Action

7. What is the relationship between capillary diameter and height of liquid column in the capillary?

8. To what height does water rise in a thin glass tube, having a 3 mm inner radius? Take the angle of contact to be 0°.

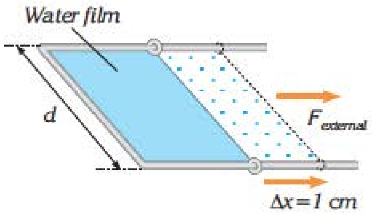
9. What is the mass of water, rising in a glass capillary having a 2 mm inner diameter? The angle of contact is 0°.

10. Show that work done by the force of surface tension, while rising a liquid in a capillary, is given by $4\pi\sigma^2/\rho g$.

11. Explain why water rises to different heights in capillaries made of different materials, even if the inner radii of the capillaries are equal.

8.4 Surface Potential Energy

12.



A film of water is stretched over a U frame by a movable section, which freely slides along the frame. What work is done in stretching the film's length by an additional length $\Delta x=1$ cm, as shown in the figure, if the width of the frame is d = 4 cm.

13. You are to peel the skins of 10 kg of potatoes. Would you prefer to work with large or small potatoes? Why?

14. What heat is released when 1000 small spherical droplets of mercury combine to form a large drop? The initial droplets are identical, each with a radius of 1 of mm.

8.5 The Exceptional behaviour of Water

15. A cube of ice floats in a glass of water. Does the water level in the glass rise or fall when the ice melts?

16. What is the temperature of water at the bottom of a 35-m deep lake, when the outside temperature is –40 °C and the thickness of the ice over the lake surface is 1.5 m?

8.6 The Molecular Structure of Solid Substances

17. What is 'allotropy'?

18. How can we explain the fact that a small cubic crystalline substance may assume a rectangular prism shape as it is heated?

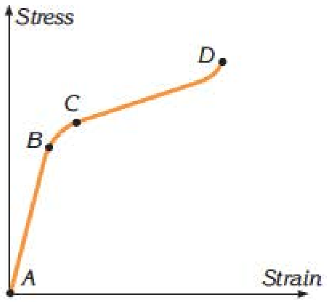
19. Why are metals isotropic the although they have a crystalline structure?

20. Can we define a latent heat of fusion for amorphous substances?

21. Show that the distance between centres of atoms in a solid is given by $\ell = \sqrt[3]{M/N_A\rho}$, where M is the molar mass, and ρ is the density of the substance.

8.7 Stress and Strain, Elasticity, Young's Modulus

22.



The figure shows a typical strain-tensile stress graph for a steel wire.

a) Where does the wire break?

b) Between which points on the graph can we define a proportionality constant?

c) Point C shows the 'elastic limit'. What happens when this limit is exceeded?

23. A wire of radius 1 mm, fixed to the ceiling at one end, carries a 20-kg load tied to its other end. What is the stress in the wire?

24. A cable has a length of 5 m and a cross-sectional area of 2.5 mm^2. The length of the cable increases by a 1-mm, as it is stretched by a 100-N force. Find:

a) Stress

b) Strain

c) Young's modulus for the cable

8.8 Hooke's Law

25. What force is needed to increase the length of a steel wire by 3 mm? The initial length of the wire is 6 m and its cross sectional area is 1 mm^2. (Take E=20×10^{10} Pa for steel)

26. The same stretching force is applied to two different wires, made of the same material. The diameter of one of the wires is twice the diameter of the other. What is the ratio of the strains in the wires?

27. A 50 kg metal ball is suspended by a steel wire of length 20-m and diameter 6-mm. What are the fractional and absolute changes in the length of the wire? (Take E=20×10^{10} Pa for steel)

28. At what load will a given metal wire of 2 cm diameter break, if its breaking limit of mechanical stress equals 1000 N/mm^2?

29. What stress value causes a strain of 0.001 in an aluminum cable? (Take E =7×10^{10} Pa for aluminum)

30. What length does a steel cable have, if it breaks under the action of its own weight when suspended freely from one end? The density of steel is 7800 kg/m^3, the breaking limit of mechanical stress is 3.2×10^8 Pa.

31. Show that the maximum possible height of a wall is given by $\frac{\sigma_{max}}{\rho g}$ where ρ is the density of the wall, g is the free-fall acceleration and σ_{max} is the maximum compressive stress the wall's material can stand.

ANSWER KEY

Chapter 1

Fluid Mechanics

1. 7.9 g/cm^3
2. Intrinsic
3. 5 dm^3, 5×10^{-3} m^3
4. 0.048 dm^3, 4.8×10^{-5} m^3
5. 800 g/dm^3
6. 370.4 cm^3
7. 510 kg
8. 900 kg/m^3
11. Pa
12. 3×10^{-5} N/cm^2
13. 0.12 atm
14. 0.92 atm, 92 kPa
16. 2125 Pa
17. 7900 Pa
19. 20 m
20. 0.1 m^2
21. 20 N
22. a) 9×10^6 N
    b) 1.35×10^6 N
23. $P_1=P_2=P_3$
    $F_1=F_2=F_3$
24. 18 000 N
25. No
26. 400 cm
27. 20 cm
28. 136 Pa
30. 1. gauge, 2. absolute
31. a) 96 cm-Hg
    b) 1.26 atm
32. 84 cm-Hg
33. 1
34. 0.7 g/cm^3
35. 1000 N
36. 600 N
37. 800 kg/m^3
38. 9×10^6 N
39. 640 N
40. 690 N
41. 6 000 kg/m^3
42. 1 333.3 N
43. Equal
44. 9×10^6 N
45. 80 kg
46. 38 000 N
47. 2 kg
48. 1.2 m^3
49. 2 cm
50. 1
51. falls
52. 1 m/s
53. 2
54. 720 kg
55. Speed increases
56. 30 cm

Chapter 2

Structure of Matter

1. Proton, neutron, electron
2. Proton 1836 times heavier
3. Exactly equal
6. Number of protons
8. 14 g
9. 42×10^{23}
10. 84×10^{23}
11. 28 g
12. 7.3×10^{-26} kg
13. 12 g
14. mercury
15. 0.032 kg/mole
21. KE >> |PE|
22. solid, liquid
23. gas

Chapter 3

Temperature and Gas Laws

1. 98.6 °F, 310.15 K
2. 233.15 K, –40 °F
3. 280 °C, 280 K
5. 30.0036 m, 29.9928 m
6. Gets larger
8. 1.2 mm
10. $\alpha_{red} > \alpha_{blue}$

11. 500.5 mm

12. 1020 °C

14. Only I

15. 120 kPa

16. 100 kPa

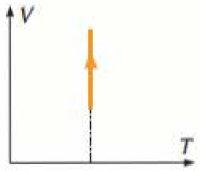
18. 24 lt

19. 200 kPa

20. 16.7 kPa

21. 80 kPa

22.



23. 24 lt

24. 20 s

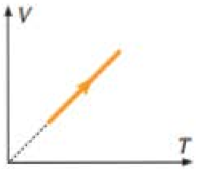
25. 75 cm-Hg

26. 92 kPa

27. 6 cm

30. Equal

31.



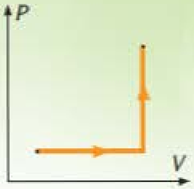
32. 53.3 cm

33. 150 K

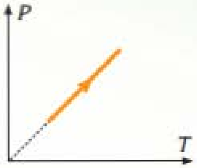
34. 500 K

35. 1/2

36.



38.



39. 133.3 kPa

40. 275 K

41. 6666.7 N

42. 3.27 atm

43. 387 °C

45. 623 250 Pa

47. 13.7 lt

48. 95.3 kg

49. 571.4 moles

50. 0.048 kg

51. 28 g/mole

52. 0.031 g

53. 1.1 kg/m^3

54. 4 atm

55. II and III

56. 498.6 kPa

57. 0.3 kg

58. 2.29 kg

59. Point 2

60. 2.07 cm^3

61. 90 kPa

62. 0.831 m

64. 2.65×10^{25} molecules/m^3

65. 103.5 kPa

68. 3.62×10^{24} molecules/m^3

Chapter 4

Heat

7. No

8. Yes. Phase change.

10. 63 min

11. 17 h 30 min

14. 1 cal/g °C = 4.2 kJ/kg °C

15. 14.4 kJ

16. 130 J/kg °C

17. 0.45 cal/°C

18. 112.5 kJ

19. No difference

20. 31 min 30 sec

21. 7560 W

22. 12 J

23. 50 kg

24. 840 m

25. 0.016 °C

26. 13.4 °C

27. 0.12 °C

28. 92.3 °C

29. 3

30. 600 g

31. 53.6 °C

32. 24.3 °C

33. 0.01 cal/g °C

40. Purity, external pressure

41. Water has more internal energy

42. 0 °C

43. 3970 J

44. 24 150 J

45. 247 kJ

46. 0.88 g/s

47. 44 min

48. 159.3 g

49. 311.8 m/s

50. 868 m/s

51. 3.87 g

52. 2.5 g

53. 20 g

54. 350 g

55. 60 min

56. 46 MJ/kg

57. 20.3 kg

58. 21 %

60. Radiation

63. 6000 W

Chapter 5

Laws of Thermodynamics

11. +380 J

12. +465 J

13. +650 J

14. +1572 J

15. +450 J

16. + 300 J

17. 0.5 lt

18. –450 kJ

19. + 1 350 J

20. + 4 487.4 J

21. +125 J

22. 1 000 cm^3

23. 10 471.6 J

24. +1800 J

25. +125 J

26. +140 J

27. +384 J

28. +4155 J

29. +1500 J

30. +9 972 J

31. +150 J

32. +37 680 J

33. T_i= 361 K, T_f=601.7 K

34. a) colder

b) 495 J

35. a) equal

b) equal

36. a) $W_1>W_2$

b) $\Delta U_1=\Delta U_2$

c) $Q_1>Q_2$

38. adiabatic

39. isobaric

40. isobaric

41. does work

42. More than twice

43. +300 J

44. –20 J

45. 0

46. a) 0

b) –112 J

47. +200 J

48. 81 kJ

49. –6.4 kJ

50. 67 kJ

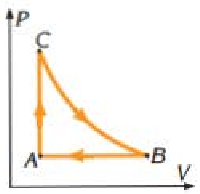
52. a) 363 400 J

b) 363 399.7 J

53. a) 400 J

b) 900 K, 1800 K, 600 K

54.



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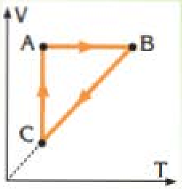

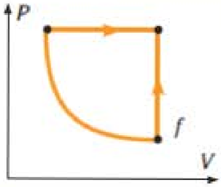

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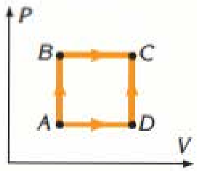

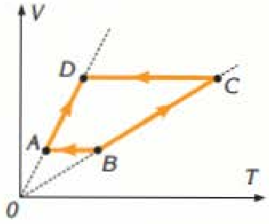

58. 33.3 %

59. 2142.9 J

60. 31.2 %

61. **a)** 4.32×10^{13} J = 12 000 MWh

b) 5.28×10^{13}J

62. 34.3%

63. 59.43 kg

64. heats

65. 5000 J

68. 63.4 %

69. 75 %

70. 400 J

71. 630 K

74. A: a,c,d,e,f

B: b

Chapter 6
Kinetic Theory of Gases

1. 42.43 m/s

2. 8.3×10^{-22} J

3. 2

5. 6×10^{-21} J

6. 200 kPa

7. 388.9 kPa

8. 4

9. 500 m/s

10. 600 m/s

11. equal

12. **a)** 6.21×10^{-21}J

b) 6.21×10^{-21}J

13. 6.21×10^{-21}J

14. Helium

15. 510.8 m/s

16. 2.65

17. 346.4 m/s

20. equal

21. oxygen

22. 18697.5 J

23. 900 J

24. 200 J

25. **a)** 6980.4 J

b) 6980.4 J

26. 600 J

27. 2493 J

28. 4155 J

29. **a)** $3/2nR\,\Delta T$

b) $5/2nR\,\Delta T$

30. 20 kJ

31. 200 J

32. 360 J

33. 8.31 kJ

34. 20 kPa

35. 7.5 J

36. $\Delta T = 12$ K

37. 0.67 moles

38. 550 J

39. $T = 293.46$ K

$P = 101.7$ kPa

40. **a)** –48J

b) 447 J

41. **a)** A–B: Q= + 290 J

B–C: Q= –1650 J

C–A: Q= +1530 J

b) $\eta = 9.3\%$

Chapter 7
Real Gases

3. 0.21 atm

4. 0.285 kg/m^3

13. 88.15%

15. 0.58 kg/m^3

21. Only (c)

28. 1902 Pa

29. 2.77 kg

30. 1.84 kg

31. 3.45 g

33. a) 0.31 m^3

34. a) 10.7 kPa
    b) 12.3 kPa
    c) 12.3 kPa

35. 2.78 g

36. 5.17 mg

37. yes

38. 15 %

39. 10.3 g/m^3

40. 1075 g

41. 32%

Chapter 8
Liquids and Solids

3. No.

8. 4.8 mm

9. 90.4 mg

12. 5.76×10^{-5} J

13. Large

14. 5.26 mJ

15. No change

16. +4 °C

23. 63.7 MPa

24. a) 40 MPa
    b) 2×10^{-4}
    c) 2×10^{11} Pa

25. 100 N

26. 4

27. $\Delta L/L = 8.85 \times 10^{-5}$
    $\Delta L = 1.77$ mm

28. 314 kN

29. 70 MPa

30. 4102 m

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